THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 10 SEPTEMBER, 1942 NUMBER 9

Vibration–Rotation Energies of Planar ZXY_2 Molecules

Part I. The Vibrational Modes and Frequencies

SAMUEL SILVER* AND EARLE S. EBERS† **
Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio
(Received June 11, 1942)

The normal modes and frequencies of planar ZXY_2 molecules are investigated using the most general potential function consistent with the symmetry. The equilibrium configuration has the symmetry of the group C_{2V} and consequently the frequencies are all non-degenerate. By developing a set of generalized coordinates having the same symmetry properties as the normal coordinates, the secular determinant is factored directly into one third-order determinant, one linear factor, and one second-order determinant.

1. INTRODUCTION

CERTAIN discrepancies exist between the interpretations of the infra-red spectra and the electronic spectra of formaldehyde.[1] Preparatory to a re-investigation of the infra-red data we felt it would be desirable to have a complete unified treatment of the vibration-rotation energies of planar ZXY_2 molecules. In the present paper we develop the normal coordinates and frequencies; in Part II we shall consider the quantum-mechanical Hamiltonian and its eigenvalues and special problems which are pertinent to the interpretation of the formaldehyde spectrum.

The vibrational frequencies have been studied previously by Lechner[2] for a valence force model and by Bernstein[3] who studied the symmetrical modes under the same type of force system. In the formulation presented here a general potential function is used so that, if desired, other force models can be investigated. Also we give the normal coordinate transformation which is needed for subsequent work.

2. THE SYMMETRY COORDINATES

We take as our system of axes the principal axes of the equilibrium configuration. The YZ plane is the plane of the molecule and the Z axis coincides with the twofold axis of symmetry. The coordinates of the equilibrium positions are designated as x_K^0, y_K^0, z_K^0 (the X atom being numbered 1, the Z atom 2, the Y atoms 3 and 4). The components of the displacement of the kth atom from its equilibrium position are x_K, y_K, z_K. The coordinate system and the symmetry elements of the molecule are shown in Fig. 1, and in Table I are listed the coordinates of the equilibrium positions.

* Now at the University of Oklahoma.
† Fellow of the Royal Society of Canada.
** Present address: U. S. Rubber Company, Development Department, Passaic, New Jersey.
[1] A brief summary of these spectra is given by H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 113 (1941).
[2] F. Lechner, Ber. Wien. Akad. Wiss. [IIa] **141**, 633 (1932).
[3] H. J. Bernstein, J. Chem. Phys. **6**, 718 (1938).

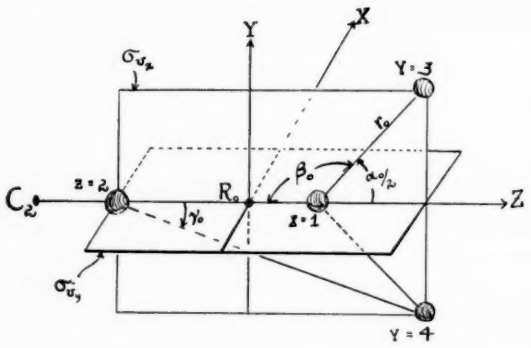


FIG. 1. The equilibrium configuration and its symmetry elements. R_0 is the Z–X distance; r_0, the X–Y distance; β_0, the ZXY angle.

The equilibrium configuration has the symmetry of the group C_{2v}. The irreducible representations of this group are given in Table II. Applying the group theory analysis of Wigner[4] and Wilson[5] we find that the normal coordinates are all non-degenerate and fall into the following symmetry classes: three, totally symmetric, transforming according to the irreducible representation A_1, one transforming according to B_1, and two transforming according to B_2. The secular equation can, therefore, be factored into one third-order factor, one linear factor, and one factor of second degree. Accordingly, we seek three symmetry coordinates belonging to class A_1, one coordinate belonging to class B_1, and two coordinates belonging to class B_2. The single coordinate of class B_1 is the normal coordinate of that symmetry type.

It is convenient to set up first the coordinates expressing infinitesimal rigid translations and rotations. These are

$$Q_\alpha{}^T=\frac{1}{M^{\frac{1}{2}}}\sum_{i=1}^{4} m_i^{\frac{1}{2}}\xi_{i\alpha}$$

$$(\alpha=x, y, z\,;\ \xi_{ix}=\xi_i,\ \xi_{iy}=\eta_i\,;\ \xi_{iz}=\zeta_i), \qquad (1)$$

and

$$Q_{\omega\alpha}=\frac{1}{(I^0_{\alpha\alpha})^{\frac{1}{2}}}\sum_{i=1}^{4} m_i^{\frac{1}{2}}(\overset{0}{x}_{i\beta}\xi_{i\gamma}-\overset{0}{x}_{i\gamma}\xi_{i\beta})$$

$$(\alpha, \beta, \gamma=x, y, \text{or } z\,;\ \overset{0}{x}_{ix}=x_i^0\,;\ \overset{0}{x}_{iy}=y_i^0, \text{etc.}), \qquad (2)$$

where we have introduced mass-reduced coordinates $\xi_{i\alpha}=m_i^{\frac{1}{2}}x_{i\alpha}$. $M=\sum m_i$ and $I^0_{\alpha\alpha}$ are the equilibrium moments of inertia. The choice of the principal axes as our coordinate system insures the orthogonality of the above coordinates. Setting $Q_\alpha{}^T=0$ and $Q_{\omega\alpha}=0$ is equivalent to using Eckart's conditions[6] when the vibrational motion is referred to rotating axes.

We require that all the symmetry coordinates be mutually orthogonal and also be orthogonal to the translational and rotational coordinates. The totally symmetric coordinates must be linear combinations of ζ_1, ζ_2, $(\zeta_3+\zeta_4)$, and $(\eta_3-\eta_4)$. The coordinates of class B_2 are linear combinations of η_1, η_2, $(\eta_3+\eta_4)$, and $(\zeta_3-\zeta_4)$. The single coordinate of class B_1 is a linear function of the ξ_i only. Except for the above restrictions, the A_1 and B_2 coordinates are completely arbitrary. We have chosen them so that, when the ZXY_2 model is reduced to the symmetrical XY_3 model, they reduce to the symmetry coordinates developed for the latter model by Silver and Shaffer.[7] We give below the inverse transformation expressing the $\xi_{i\alpha}$ in terms of the symmetry coordinates. To get the

TABLE I. Coordinates of the equilibrium positions.

k	$x_k{}^0$	$y_k{}^0$	$z_k{}^0$
1	0	0	$\dfrac{m_Z R_0+2m_Y r_0\cos\beta_0}{M}$
2	0	0	$\dfrac{2m_Y r_0\cos\beta_0-(m_X+2m_Y)R_0}{M}$
3	0	$r_0\sin\beta_0$	$\dfrac{m_Z R_0-(m_X+m_Z)r_0\cos\beta_0}{M}$
4	0	$-r_0\sin\beta_0$	

$M=m_X+m_Z+2m_Y$.

TABLE II. Irreducible representations of the group C_{2v}.

	E	C_2	σv_z	σv_y
A_1; z	1	1	1	1
B_1; x	1	−1	−1	1
A_2	1	1	−1	−1
B_2; y	1	−1	1	−1

[4] E. Wigner, Göttingen Nachrichten, p. 133 (1930).
[5] E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).
[6] C. Eckart, Phys. Rev. **47**, 552 (1935).
[7] S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

latter explicitly, simply interchange rows and columns.

$$\xi_1=\left(\frac{2m_Ym_Z}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_3^0-z_2^0)Q_6\,;\quad \xi_2=\left(\frac{2m_Xm_Y}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_1^0-z_3^0)Q_6\,;\quad \xi_3=\xi_4=\left(\frac{m_Xm_Z}{2MI^0_{yy}}\right)^{\frac{1}{2}}(z_2^0-z_1^0)Q_6. \tag{3a}$$

$$\eta_1=\left(\frac{2m_Ym_Z}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_3^0-z_2^0)S_4+\left(\frac{m_XI^0_{zz}}{I^0_{yy}I^0_{xx}}\right)^{\frac{1}{2}}z_1^0S_5\,;$$

$$\eta_2=\left(\frac{2m_Xm_Y}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_1^0-z_3^0)S_4+\left(\frac{m_ZI^0_{zz}}{I^0_{yy}I^0_{xx}}\right)^{\frac{1}{2}}z_2^0S_5\,;$$

$$\left.\begin{matrix}\eta_3\\ \eta_4\end{matrix}\right\}=\begin{matrix}+\\ -\end{matrix}\left[\frac{m_Z^{\frac{1}{2}}\sin\beta_0}{[2(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_1-\cos\beta_0\left[\frac{m_Z+2m_Y}{2(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}S_3\right]$$
$$+\left(\frac{m_Xm_Z}{2mI^0_{yy}}\right)^{\frac{1}{2}}(z_2^0-z_1^0)S_4+\left(\frac{m_YI^0_{zz}}{I^0_{xx}I^0_{yy}}\right)^{\frac{1}{2}}z_3^0S_5. \tag{3b}$$

$$\zeta_1=\left[\frac{m_Z+2m_Y}{M}\right]^{\frac{1}{2}}S_2\,;$$

$$\zeta_2=\frac{2m_Y^{\frac{1}{2}}\cos\beta_0}{[2(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_1-\left[\frac{m_Xm_Z}{M(m_Z+2m_Y)}\right]^{\frac{1}{2}}S_2+\frac{2(m_Ym_Z^{\frac{1}{2}})\sin\beta_0}{[2(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_3\,;$$

$$\left.\begin{matrix}\zeta_3\\ \zeta_4\end{matrix}\right\}=-\frac{m_Z^{\frac{1}{2}}\cos\beta_0}{[2(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_1-\left[\frac{m_Xm_Y}{M(m_Z+2m_Y)}\right]^{\frac{1}{2}}S_2$$
$$-\frac{m_Z\sin\beta_0}{[2(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_3\pm\left(\frac{I^0_{yy}}{2I^0_{xx}}\right)^{\frac{1}{2}}S_5. \tag{3c}$$

S_1, S_2, S_3 are the totally symmetric coordinates; they reduce to Q_1, S_{2a}, and S_{4a} of the XY_3 case, respectively. S_4 and S_5 are of class B_2 and reduce to S_{2b} and S_{4b} of the XY_3 problem. Q_6 is unique; it corresponds to Q_3 of the XY_3 molecule, representing the bending of the plane of the molecule. The coordinates are all normalized to unity. It is readily verified that, because the symmetry coordinates are orthogonal to the translational and rotational coordinates, the $\xi_{i\alpha}$ satisfy Eckart's conditions.

3. THE POTENTIAL ENERGY

Let δr_{ij} be the changes in the $Z-X$ and $X-Y_i$ distances, δq_{ij} be the variations in the $Z-Y_i$ and Y_i-Y_j distances. The most general quadratic potential consistent with the symmetry is

$$2V=K_1\delta r_{12}^2+K_2(\delta r_{13}^2+\delta r_{14}^2)+K_3(\delta q_{23}^2+\delta q_{24}^2)+K_4\delta q_{34}^2+2K_5\delta r_{12}(\delta r_{13}+\delta r_{14})$$
$$+2K_6\delta r_{12}(\delta q_{23}+\delta q_{24})+2K_7\delta r_{12}\delta q_{34}+2K_8\delta r_{13}\delta r_{14}+2K_9(\delta r_{13}\delta q_{23}+\delta r_{14}\delta q_{24})$$
$$+2K_{10}(\delta r_{13}\delta q_{24}+\delta r_{14}\delta q_{23})+2K_{11}(\delta r_{13}+\delta r_{14})\delta q_{34}+2K_{12}\delta q_{23}\delta q_{24}+2K_{13}(\delta q_{23}+\delta q_{24})\delta q_{34}. \tag{4}$$

This does not include the energy associated with the bending of the plane of the molecule. The same difficulty arises in all planar molecules, since for the latter type of deformation the δr_{ij} and δq_{ij} are zero to the first order of infinitesimals. It is necessary to add a special term for this motion. Since Q_6 is the normal coordinate for this vibrational mode, we can write for the potential energy associated with the bending of the plane of the molecule

$$V_{B_1}=(k_{66}/2)Q_6^2. \tag{5}$$

Returning to (4), we express V in terms of the symmetry coordinates by calculating the δr_{ij} and δq_{ij} in terms of them and substituting into (4). The labor is considerably reduced by considering

the A_1 and B_2 modes separately. In the totally symmetric modes we have

$$\delta r_{13}=\delta r_{14},\quad \delta q_{23}=\delta q_{24}=\delta r_{12}\cos\gamma_0-\frac{\cos\gamma_0}{\cos\beta_0}\delta r_{13}+\frac{1}{2}\frac{\sin(\beta_0+\gamma_0)}{\cos\beta_0}\delta q_{34}.$$

For these modes the potential energy reduces to

$$2V_{A1}=\Lambda_{11}\delta r_{12}^2+\Lambda_{22}\delta r_{13}^2+\Lambda_{33}\delta q_{34}^2+2\Lambda_{12}\delta r_{12}\delta r_{13}+2\Lambda_{13}\delta r_{12}\delta q_{34}+2\Lambda_{23}\delta r_{13}\delta q_{34}, \tag{6}$$

where

$$\begin{aligned}
\Lambda_{11}&=K_1+2(K_3+K_{12})\cos^2\gamma_0+4K_6\cos\gamma_0,\\
\Lambda_{22}&=2(K_2+K_8)+2(K_3+K_{12})\cos^2\gamma_0/\cos^2\beta_0-4(K_9+K_{10})\cos\gamma_0/\cos\beta_0,\\
\Lambda_{33}&=K_4+(K_3+K_{12})\sin^2(\beta_0+\gamma_0)/2\cos^2\beta_0+2K_{13}\sin(\beta_0+\gamma_0)/\cos\beta_0,\\
\Lambda_{12}&=2K_5-2(K_3+K_{12})\frac{\cos^2\gamma_0}{\cos\beta_0}-2K_6\frac{\cos\gamma_0}{\cos\beta_0}+2(K_9+K_{10})\cos\gamma_0,\\
\Lambda_{13}&=K_7+(K_3+K_{12})\frac{\sin(\beta_0+\gamma_0)\cos\gamma_0}{\cos\beta_0}+K_6\frac{\sin(\beta_0+\gamma_0)}{\cos\beta_0}+2K_{13}\cos\gamma_0,\\
\Lambda_{23}&=2K_{11}-(K_3+K_{12})\frac{\sin(\beta_0+\gamma_0)\cos\gamma_0}{\cos^2\beta_0}+(K_9+K_{10})\frac{\sin(\beta_0+\gamma_0)}{\cos\beta_0}-2K_{13}\cos\gamma_0/\cos\beta_0.
\end{aligned} \tag{7}$$

Calculating δr_{12}, δr_{13}, and δq_{34} in terms of S_1, S_2, and S_3, and substituting into (6), we obtain

$$2V_{A1}=k_{11}S_1^2+k_{22}S_2^2+k_{33}S_3^2+2k_{12}S_1S_2+2k_{13}S_1S_3+2k_{23}S_2S_3, \tag{8}$$

where

$$\begin{aligned}
k_{11}&=\frac{1}{m_Z+2m_Y\cos^2\beta_0}\left\{\frac{2m_Y\cos^2\beta_0}{m_Z}\Lambda_{11}+\frac{m_Z}{2m_Y}\Lambda_{22}+\frac{2m_Z\sin^2\beta_0}{m_Y}\Lambda_{33}\right.\\
&\qquad\left.-2\cos\beta_0\Lambda_{12}-4\sin\beta_0\cos\beta_0\Lambda_{13}+\frac{2m_Z\sin\beta_0}{m_Y}\Lambda_{23}\right\};\\
k_{22}&=\frac{M}{m_X(m_Z+2m_Y)}\{\Lambda_{11}+\Lambda_{22}\cos^2\beta_0+2\Lambda_{12}\cos\beta_0\};\\
k_{33}&=\frac{1}{m_Z+2m_Y\cos^2\beta_0}\left\{\frac{2m_Y\sin^2\beta_0}{m_Z+2m_Y}\Lambda_{11}+\frac{2m_Y\sin^2\beta_0\cos^2\beta_0}{m_Z+2m_Y}\Lambda_{22}+\frac{2(m_Z+2m_Y)\cos^2\beta_0}{m_Y}\Lambda_{33}\right.\\
&\qquad\left.+\frac{4m_Y\sin^2\beta_0\cos\beta_0}{m_Z+2m_Y}\Lambda_{12}+4\sin\beta_0\cos\beta_0\Lambda_{13}+4\sin\beta_0\cos^2\beta_0\Lambda_{23}\right\};\\
k_{12}&=\frac{M^{\frac{1}{2}}}{[2m_Xm_Ym_Z(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}\{-2m_Y\cos\beta_0\Lambda_{11}+m_Z\cos\beta_0\Lambda_{22}\\
&\qquad+(m_Z-2m_Y\cos^2\beta_0)\Lambda_{12}+2m_Z\sin\beta_0\Lambda_{13}+2m_Z\sin\beta_0\cos\beta_0\Lambda_{23}\};\\
k_{13}&=\frac{1}{(m_Z+2m_Y\cos^2\beta_0)[m_Z(m_Z+2m_Y)]^{\frac{1}{2}}}\left\{2m_Y\sin\beta_0\cos\beta_0\Lambda_{11}-m_Z\sin\beta_0\cos\beta_0\Lambda_{22}\right.\\
&\qquad-\frac{2m_Z(m_Z+2m_Y)}{m_Y}\sin\beta_0\cos\beta_0\Lambda_{33}-(m_Z-2m_Y\cos^2\beta_0)\sin\beta_0\Lambda_{12}\\
&\qquad\left.+2[(m_Z+2m_Y)\cos^2\beta_0-m_Z\sin^2\beta_0]\Lambda_{13}-\frac{m_Z\cos\beta_0[m_Z+2m_Y(1+\sin^2\beta_0)]}{m_Y}\Lambda_{23}\right\};\\
k_{23}&=\frac{-M^{\frac{1}{2}}}{(m_Z+2m_Y)[2m_Xm_Y(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}\{2m_Y\sin\beta_0\Lambda_{11}+2m_Y\sin\beta_0\cos^2\beta_0\Lambda_{22}\\
&\qquad+4m_Y\sin\beta_0\cos\beta_0\Lambda_{12}+2(m_Z+2m_Y)\cos\beta_0\Lambda_{13}+2(m_Z+2m_Y)\cos^2\beta_0\Lambda_{23}\}.
\end{aligned} \tag{9}$$

In the B_2 modes we have

$$\delta r_{12}=0\,;\quad \delta r_{13}=-\delta r_{14}\,;\quad \delta q_{23}=-\delta q_{24}\,;\quad \delta q_{34}=0,$$

whence,

$$2V_{B_2}=2(K_2-K_8)\delta r_{13}^2+2(K_3-K_{12})\delta q_{23}^2+4(K_9-K_{10})\delta r_{13}\delta q_{23}. \tag{10}$$

Calculating δr_{13} and δq_{23} in terms of S_4 and S_5 and substituting into (10), we obtain

$$2V_{B_2}=k_{44}S_4^2+k_{55}S_5^2+2k_{45}S_4S_5, \tag{11}$$

where

$$k_{44}=\frac{M}{m_Y I^0_{yy}}\left\{\frac{m_Z(z_2^0)^2\sin^2\beta_0}{m_X}(K_2-K_8)+\frac{m_X}{m_Z}(z_1^0\sin\gamma_0)^2(K_3-K_{12})-2z_1^0z_2^0\sin\gamma_0\sin\beta_0(K_9-K_{10})\right\};$$

$$k_{55}=\frac{I^0_{xx}}{m_Y I^0_{yy}}\{\cos^2\beta_0(K_2-K_8)+\cos^2\gamma_0(K_3-K_{12})-2\cos\beta_0\cos\gamma_0(K_9-K_{10})\};$$

$$k_{45}=-\frac{1}{m_Y I^0_{yy}}\left(\frac{MI^0_{xx}}{m_Xm_Z}\right)^{\frac{1}{2}}\{m_Zz_2^0\sin\beta_0\cos\beta_0(K_2-K_8)+m_Xz_1^0\sin\gamma_0\cos\gamma_0(K_3-K_{12})$$
$$-[m_Zz_2^0\sin\beta_0\cos\gamma_0+m_Xz_1^0\sin\gamma_0\cos\beta_0](K_9-K_{10})\}. \tag{12}$$

The Simple Valence Potential

The simple valence potential has found wide applicability as a starting point in the analysis of the vibrational frequencies of organic molecules. Accordingly, we give below the relations between the valence force constants and the generalized constants in the potential energy of the planar ZXY_2 molecule. For the latter molecule, the valence potential has the form

$$2V=k_{XZ}\delta r_{12}^2+k_{XY}(\delta r_{13}^2+\delta r_{14}^2)+k_{ZXY}(\delta\beta_1^2+\delta\beta_2^2)+k_{YXY}\delta\alpha^2, \tag{13}$$

where the deformation constants k_{ZXY} and k_{YXY} have dimensions of ergs/(radians)^2. Considering the A_1 and B_2 modes separately, as was done above, (13) is readily transformed into the general forms (6) and (10), respectively. In this way, we obtain

$$\Lambda_{11}=k_{XZ},$$
$$\Lambda_{22}=2k_{XY}+\frac{4\tan^2\beta_0}{r_0^2}\left(k_{YXY}+\frac{k_{ZXY}}{2}\right),$$
$$\Lambda_{33}=\frac{1}{r_0^2\cos^2\beta_0}\left(k_{YXY}+\frac{k_{ZXY}}{2}\right),$$
$$\Lambda_{12}=\Lambda_{13}=0,$$
$$\Lambda_{23}=-\frac{2\tan\beta_0}{r_0^2\cos\beta_0}\left(k_{YXY}+\frac{k_{ZXY}}{2}\right); \tag{14}$$

and

$$K_2-K_8=k_{XY}+k_{ZXY}\left\{\frac{R_0\cos\beta_0-r_0}{R_0r_0\sin\beta_0}\right\}^2,$$
$$K_3-K_{12}=\frac{k_{ZXY}}{R_0^2\sin^2\gamma_0},$$
$$K_9-K_{10}=\frac{k_{ZXY}(R_0\cos\beta_0-r_0)}{R_0^2r_0\sin\beta_0}. \tag{15}$$

4. THE SECULAR EQUATIONS

Since the symmetry coordinates are orthogonal and are normalized to unity, the kinetic energy expressed in terms of them is a sum of squares:

$$T=\tfrac{1}{2}(\dot{S}_1^2+\dot{S}_2^2+\dot{S}_3^2)+\tfrac{1}{2}\dot{Q}_6^2+\tfrac{1}{2}(\dot{S}_4^2+\dot{S}_5^2). \tag{16}$$

The frequencies are the roots of the secular determinants

$$|k_{ij}-\lambda\delta_{ij}|=0\,;\quad \lambda=4\pi^2\nu^2c^2. \tag{17}$$

It is directly evident that Q_6 is the normal coordinate of class B_1, corresponding to the frequency (in wave numbers)

$$\nu_6=\frac{1}{2\pi c}\sqrt{k_{66}}. \tag{18}$$

The totally symmetric coordinates give rise to a third-order determinantal equation; the frequencies are the roots of the cubic,

$$\lambda^3-(k_{11}+k_{22}+k_{33})\lambda^2+(k_{11}k_{22}+k_{11}k_{33}+k_{22}k_{33}-k_{13}^2-k_{12}^2-k_{23}^2)\lambda$$
$$+k_{11}k_{23}^2+k_{22}k_{13}^2+k_{33}k_{12}^2-2k_{12}k_{13}k_{23}-k_{11}k_{22}k_{33}=0. \tag{19}$$

Let λ_1, λ_2, λ_3 be the roots and Q_1, Q_2, Q_3 be the respective normal coordinates. The transformation from the symmetry coordinates to the normal coordinates is then,

$$\begin{pmatrix}S_1\\S_2\\S_3\end{pmatrix}=\begin{pmatrix}l_{11}&l_{12}&l_{13}\\l_{21}&l_{22}&l_{23}\\l_{31}&l_{32}&l_{33}\end{pmatrix}\begin{pmatrix}Q_1\\Q_2\\Q_3\end{pmatrix}, \tag{20}$$

where

$$l_{1k}=\frac{k_{13}(k_{22}-\lambda_k)-k_{12}k_{23}}{D_k};\quad l_{2k}=\frac{k_{23}(k_{11}-\lambda_k)-k_{12}k_{13}}{D_k};\quad l_{3k}=\frac{k_{12}^2-(k_{11}-\lambda_k)(k_{22}-\lambda_k)}{D_k}, \tag{21}$$

with

$$D_k=\{[k_{13}(k_{22}-\lambda_k)-k_{12}k_{23}]^2+[k_{23}(k_{11}-\lambda_k)-k_{12}k_{13}]^2+[(k_{11}-\lambda_k)(k_{22}-\lambda_k)-k_{12}^2]^2\}^{\frac{1}{2}}.$$

The B_2 frequencies are obtained from the roots of the quadratic equation

$$\lambda^2-(k_{44}+k_{55})\lambda+k_{44}k_{55}-k_{45}^2=0. \tag{22}$$

Denoting these frequencies as ν_4 and ν_5, we have

$$\nu_{4,5}=\frac{1}{2\pi c}\left\{\frac{k_{44}+k_{55}}{2}\pm\left[\left(\frac{k_{44}-k_{55}}{2}\right)^2+k_{45}^2\right]^{\frac{1}{2}}\right\}^{\frac{1}{2}}. \tag{23}$$

The transformation from S_4 and S_5 to the corresponding normal coordinates Q_4 and Q_5 is

$$S_4=l_{44}Q_4+l_{45}Q_5,\quad S_5=l_{54}Q_4+l_{55}Q_5, \tag{24}$$

where

$$l_{44}=l_{55}=\frac{k_{45}}{[(k_{44}-\lambda_4)^2+k_{45}^2]^{\frac{1}{2}}};\quad l_{45}=-l_{54}=\frac{k_{44}-\lambda_4}{[(k_{44}-\lambda_4)^2+k_{45}^2]^{\frac{1}{2}}}. \tag{25}$$

Vibration-Rotation Energies of Planar ZXY_2 Molecules

Part II. The Quantum-Mechanical Hamiltonian and the Energy Values[1]

SAMUEL SILVER
Mendenhall Laboratory of Physics, The Ohio State University, Columbus, Ohio, and Department of Physics, University of Oklahoma, Norman, Oklahoma*

(Received June 11, 1942)

Nielsen's treatment of the vibration-rotation energies of a general polyatomic molecule is applied to the planar ZXY_2 molecular model. Due to the low symmetry of the model, the vibrational modes are non-degenerate, and, if the frequencies are well separated in their values, Nielsen's general formulation can be applied directly. For this case the elements of the secular equation are evaluated to include all the first- and second-order terms in the Hamiltonian. With the view of applying the theory to the analysis of the fundamental bands of formaldehyde, the effect of an approximate degeneracy between a pair of perpendicular vibrations, of symmetry types B_1 and B_2, respectively, is considered. For this case, the vibration-rotation energies of the states giving rise to the fundamental bands are investigated to the first order of approximation. It is shown how, by a modification of Nielsen's general treatment, the secular equations can be set up with little difficulty to include all the first-order terms in the Hamiltonian. The secular equations for values of $J=0, 1, 2, 3, 4$ are given explicitly.

THE quantum-mechanical calculation of the vibration-rotation energies and the associated spectra of planar ZXY_2 molecules has been carried out previously subject to a number of simplifying assumptions.[2] Recently Nielsen[3] expanded the Wilson-Howard Hamiltonian for the vibration-rotation energies of a general polyatomic molecule and delineated a procedure for evaluating the energies to the second order of approximation. In the present paper the general treatment is applied to the planar ZXY_2 model and the constants appearing in the elements of the secular equation are evaluated in terms of the coefficients of the normal coordinate transformation, developed in the preceding paper (Part I), and the coefficients of the cubic and quartic anharmonic terms in the potential energy.

1. THE QUANTUM-MECHANICAL HAMILTONIAN†

The quantum-mechanical Hamiltonian for the system, arranged in terms according to orders of magnitude, is

$$H_0=\frac{1}{2}\left(\frac{P_x^2}{I^0_{xx}}+\frac{P_y^2}{I^0_{yy}}+\frac{P_z^2}{I^0_{zz}}\right)+\frac{1}{2}\sum_{k=1}^{6}h\omega_k\left(\frac{p_{q_k}^2}{\hbar^2}+q_k^2\right);\quad \omega_k=2\pi c\nu_k. \tag{1a}$$

$$H_1=-\frac{ih^{\frac{1}{2}}}{4}\sum_{k=1}^{3}\sigma_k p_{q_k}-\frac{h^{\frac{1}{2}}}{2}\sum_{k=1}^{3}\left[a_k\frac{P_x^2}{I^{0\,2}_{xx}}+b_k\frac{P_y^2}{I^{0\,2}_{yy}}+c_k\frac{P_z^2}{I^{0\,2}_{zz}}\right]q_k/\omega_k^{\frac{1}{2}}$$
$$+\frac{h^{\frac{1}{2}}}{2I^0_{yy}I^0_{zz}}(P_yP_z+P_zP_y)\sum_{k=4}^{5}e_kq_k/\omega_k^{\frac{1}{2}}-\left[\frac{p_xP_x}{I^0_{xx}}+\frac{p_yP_y}{I^0_{yy}}+\frac{p_zP_z}{I^0_{zz}}\right]+U_1. \tag{1b}$$

$$H_2=-\frac{ih}{2}\sum_{k=1}^{6}s_{kk}q_kp_{q_k}+\frac{1}{2}\sum_{k=1}^{6}\frac{\hbar}{\omega_k}q_k^2\left[\epsilon_{xk}\frac{P_x^2}{I^{0\,2}_{xx}}+\epsilon_{yk}\frac{P_y^2}{I^{0\,2}_{yy}}+\epsilon_{zk}\frac{P_z^2}{I^{0\,2}_{zz}}\right]+\frac{1}{2}\left(\frac{p_x^2}{I^0_{xx}}+\frac{p_y^2}{I^0_{yy}}+\frac{p_z^2}{I^0_{zz}}\right)+U_2, \tag{1c}$$

[1] This paper was presented at the meeting of Section B, The American Association for the Advancement of Science, held in Dallas, December, 1941. Abstract, Phys. Rev. **61**, 383 (1942).

* The work covered by this and the preceding paper was initiated at the Ohio State University while the author was in residence there during 1940–1941.

[2] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931); J. Chem. Phys. **5**, 818 (1937); Phys. Rev. **55**, 289 (1939).

[3] H. H. Nielsen, Phys. Rev. **60**, 794 (1941).

† Only the essential results are given here. For the details of the development of the Hamiltonian, the reader is referred to reference 3 above.

plus terms which make no contribution to the second order of approximation. q_k is related to the normal coordinate Q_k by $q_k=(\omega_k/\hbar)^{\frac{1}{2}}Q_k$; p_k is the momentum conjugate to q_k; U_1 and U_2 are the cubic and quartic anharmonic terms in the potential energy. From the symmetry properties of the normal coordinates (and hence, the q_k), it is seen that the most general forms for U_1 and U_2 are

$$\begin{aligned}U_1=hc\{&\beta_{111}q_1^3+\beta_{222}q_2^3+\beta_{333}q_3^3+\beta_{112}q_1^2q_2+\beta_{113}q_1^2q_3+\beta_{221}q_2^2q_1+\beta_{223}q_2^2q_3+\beta_{331}q_3^2q_1+\beta_{332}q_3^2q_2\\&+\beta_{441}q_4^2q_1+\beta_{442}q_4^2q_2+\beta_{443}q_4^2q_3+\beta_{551}q_5^2q_1+\beta_{552}q_5^2q_2+\beta_{553}q_5^2q_3+\beta_{661}q_6^2q_1+\beta_{662}q_6^2q_2\\&+\beta_{663}q_6^2q_3+\beta_{123}q_1q_2q_3+\beta_{145}q_1q_4q_5+\beta_{245}q_2q_4q_5+\beta_{345}q_3q_4q_5\},\end{aligned}\tag{2}$$

$$\begin{aligned}U_2=hc\{&\sum_{k=1}^{6}\gamma_{kkkk}q_k^4+\gamma_{1112}q_1^3q_2+\gamma_{1113}q_1^3q_3+\gamma_{2221}q_2^3q_1+\gamma_{2223}q_2^3q_3+\gamma_{3331}q_3^3q_1+\gamma_{3332}q_3^3q_2\\&+\gamma_{4445}q_4^3q_5+\gamma_{5554}q_5^3q_4+\gamma_{1122}q_1^2q_2^2+\gamma_{1133}q_1^2q_3^2+\gamma_{1144}q_1^2q_4^2+\gamma_{1155}q_1^2q_5^2+\gamma_{1166}q_1^2q_6^2\\&+\gamma_{2233}q_2^2q_3^2+\gamma_{2244}q_2^2q_4^2+\gamma_{2255}q_2^2q_5^2+\gamma_{2266}q_2^2q_6^2+\gamma_{3344}q_3^2q_4^2+\gamma_{3355}q_3^2q_5^2+\gamma_{3366}q_3^2q_6^2\\&+\gamma_{4455}q_4^2q_5^2+\gamma_{4466}q_4^2q_6^2+\gamma_{5566}q_5^2q_6^2+\gamma_{1233}q_1q_2q_3^2+\gamma_{1244}q_1q_2q_4^2+\gamma_{1255}q_1q_2q_5^2+\gamma_{1266}q_1q_2q_6^2\\&+\gamma_{1322}q_1q_3q_2^2+\gamma_{1344}q_1q_3q_4^2+\gamma_{1355}q_1q_3q_5^2+\gamma_{1366}q_1q_3q_6^2+\gamma_{2311}q_2q_3q_1^2+\gamma_{2344}q_2q_3q_4^2\\&+\gamma_{2355}q_2q_3q_5^2+\gamma_{2366}q_2q_3q_6^2+\gamma_{1145}q_1^2q_4q_5+\gamma_{2245}q_2^2q_4q_5+\gamma_{3345}q_3^2q_4q_5+\gamma_{6645}q_6^2q_4q_5\\&+\gamma_{1245}q_1q_2q_4q_5+\gamma_{1345}q_1q_3q_4q_5+\gamma_{2345}q_2q_3q_4q_5\}.\end{aligned}\tag{3}$$

Although the coordinates q_4 and q_5 cannot appear singly in the first degree, the product term q_4q_5 is admissible since both coordinates transform in the same way under the operations of the symmetry group.

The operators p_x, p_y, p_z are the components of the vibrational angular momentum and are given by:

$$\begin{aligned}p_x&=\sum_{k=1}^{3}\left\{\zeta_{k4}\left[\left(\frac{\nu_k}{\nu_4}\right)^{\frac{1}{2}}q_4p_{q_k}-\left(\frac{\nu_4}{\nu_k}\right)^{\frac{1}{2}}q_kp_{q_4}\right]+\zeta_{k5}\left[\left(\frac{\nu_k}{\nu_5}\right)^{\frac{1}{2}}q_5p_{q_k}-\left(\frac{\nu_5}{\nu_k}\right)^{\frac{1}{2}}q_kp_{q_5}\right]\right\},\\p_y&=\sum_{k=1}^{3}\left\{\zeta_{k6}\left[\left(\frac{\nu_6}{\nu_k}\right)^{\frac{1}{2}}q_kp_{q_6}-\left(\frac{\nu_k}{\nu_6}\right)^{\frac{1}{2}}q_6p_{q_k}\right]\right\},\\p_z&=\sum_{k=4}^{5}\left\{\zeta_{k6}\left[\left(\frac{\nu_k}{\nu_6}\right)^{\frac{1}{2}}q_6p_{q_k}-\left(\frac{\nu_6}{\nu_k}\right)^{\frac{1}{2}}q_kp_{q_6}\right]\right\}.\end{aligned}\tag{4}$$

The constants appearing in H are defined by

$$\sigma_k=\omega_k^{\frac{1}{2}}\left(\frac{a_k}{I^0_{xx}}+\frac{b_k}{I^0_{yy}}+\frac{c_k}{I^0_{zz}}\right),$$

$$s_{kk}=\frac{A_{kk}}{I^0_{xx}}+\frac{B_{kk}}{I^0_{yy}}+\frac{C_{kk}}{I^0_{zz}}-\frac{1}{2}\left(\frac{a_k^2}{I^{0\,2}_{xx}}+\frac{b_k^2}{I^{0\,2}_{yy}}+\frac{c_k^2}{I^{0\,2}_{zz}}\right),\quad k=1,2,3$$

$$s_{kk}=\frac{A_{kk}}{I^0_{xx}}+\frac{B_{kk}}{I^0_{yy}}+\frac{C_{kk}}{I^0_{zz}}-\frac{e_k^2}{I^0_{yy}I^0_{zz}},\quad k=4,5$$

$$s_{66}=\frac{B_{66}}{I^0_{yy}}+\frac{C_{66}}{I^0_{zz}},$$

$$\epsilon_{zk}=\frac{a_k^2}{I^0_{xx}}-A_{kk};\quad \epsilon_{yk}=\frac{b_k^2}{I^0_{yy}}-B_{kk}+\frac{e_k^2}{I^0_{zz}};\quad \epsilon_{zk}=\frac{c_k^2}{I^0_{zz}}-C_{kk}+\frac{e_k^2}{I^0_{yy}},\tag{5}$$

where

$$a_k=2\left\{\left[\frac{2m_Ym_Z}{m_Z+2m_Y\cos^2\beta_0}\right]^{\frac{1}{2}}(r_0-R_0\cos\beta_0)l_{1k}+\left[\frac{m_XM}{m_Z+2m_Y}\right]^{\frac{1}{2}}z_1{}^0l_{2k}\right.$$
$$\left.-\left[\frac{2m_Y}{(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}Mz_1{}^0\sin\beta_0l_{3k}\right\},\quad k=1,2,3$$

$$b_k=2\left\{\left[\frac{2m_Ym_Z}{m_Z+2m_Y\cos^2\beta_0}\right]^{\frac{1}{2}}(z_2{}^0-z_3{}^0)\cos\beta_0l_{1k}+\left[\frac{m_XM}{m_Z+2m_Y}\right]^{\frac{1}{2}}z_1{}^0l_{2k}\right. \tag{6a}$$
$$\left.+m_Z\left[\frac{2m_Y}{(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}(z_2{}^0-z_3{}^0)\sin\beta_0l_{3k}\right\},\quad k=1,2,3$$

$$c_k=2\left\{\left[\frac{2m_Ym_Z}{m_Z+2m_Y\cos^2\beta_0}\right]^{\frac{1}{2}}y_3{}^0\sin\beta_0l_{1k}-\left[\frac{2m_Y(m_Z+2m_Y)}{m_Z+2m_Y\cos^2\beta_0}\right]^{\frac{1}{2}}y_3{}^0\cos\beta_0l_{3k}\right\},\quad k=1,2,3$$

$a_k=b_k=c_k=0,\quad (k>3);\quad e_k=0,\quad (k=1,2,3,6);\quad e_k=2[I^0_{yy}I^0_{zz}/I^0_{xx}]^{\frac{1}{2}}l_{5k},\quad (k=4,5).$

$A_{kk}=1-(\zeta^2_{k4}+\zeta^2_{k5}),\quad (k=1,2,3);\quad A_{kk}=1-\sum_{j=1}^{3}\zeta^2_{jk},\quad (k=4,5);\quad A_{66}=0,$

$$B_{kk}=\left\{\frac{(m_Z+2m_Y)\cos^2\beta_0}{m_Z+2m_Y\cos^2\beta_0}l^2_{1k}+\frac{m_X}{M}l^2_{2k}+\frac{m_Z\sin^2\beta_0}{m_Z+2m_Y\cos^2\beta_0}l^2_{3k}\right.$$
$$\left.+\frac{2[m_Z(m_Z+2m_Y)]^{\frac{1}{2}}}{m_Z+2m_Y\cos^2\beta_0}\sin\beta_0\cos\beta_0l_{1k}l_{3k}\right\}-\zeta^2_{k6},\quad (k=1,2,3) \tag{6b}$$

$B_{kk}=(I^0_{yy}/I^0_{xx})l^2_{5k},\quad (k=4,5);\quad B_{66}=1-\sum_{j=1}^{3}\zeta^2_{j6};$

$C_{kk}=1-B_{kk}-\zeta^2_{k6},\quad (k=1\cdots5);\quad C_{66}=1-(\zeta^2_{46}+\zeta^2_{56}),$

with

$$\zeta_{kj}=\left[\frac{Mm_X}{I^0_{yy}(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0\cos\beta_0l_{1k}l_{4j}+M\left[\frac{m_Z}{I^0_{xx}I^0_{yy}(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0z_2{}^0\sin\beta_0l_{1k}l_{5j}$$
$$+\left[\frac{2m_Ym_Z}{I^0_{yy}(m_Z+2m_Y)}\right]^{\frac{1}{2}}(z_3{}^0-z_2{}^0)l_{2k}l_{4j}+\left[\frac{Mm_XI^0_{zz}}{I^0_{xx}I^0_{yy}(m_Z+2m_Y)}\right]^{\frac{1}{2}}z_1{}^0l_{2k}l_{5j}$$
$$+\left[\frac{m_Xm_ZM}{I^0_{yy}(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0\sin\beta_0l_{3k}l_{4j}$$
$$+\frac{MI^0_{yy}z_1{}^0+m_zI^0_{zz}(z_2{}^0-z_3{}^0)}{r_0[I^0_{xx}I^0_{yy}(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}l_{3k}l_{5j},\quad (k=1,2,3;\ j=4,5) \tag{7}$$

$$\zeta_{k6}=\left[\frac{m_XM}{I^0_{yy}(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0\cos\beta_0l_{1k}+\left[\frac{2m_Ym_Z}{I^0_{yy}(m_Z+2m_Y)}\right]^{\frac{1}{2}}(z_3{}^0-z_2{}^0)l_{2k}$$
$$+\left[\frac{m_Xm_ZM}{I^0_{yy}(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0\sin\beta_0l_{3k},\quad (k=1,2,3)$$

$\zeta_{k6}=l_{4k},\quad (k=4,5).$

The coefficients l_{kj} and the equilibrium coordinates $z_k{}^0$ are given in Part I.

2. TRANSFORMATION OF THE HAMILTONIAN AND THE ENERGY VALUES

Shaffer, Nielsen, and Thomas[4] have shown that the perturbation calculation can be simplified to a considerable extent by applying a contact transformation to the operator H, $H'=THT^{-1}$, which carries terms of first order in H into second-order terms in H'. Details of the method are to be found in the paper by SNT; a table of the operators comprising the transformation function T, appropriate for the coordinates used here, has been published by Silver and Shaffer.[5]

Due to the low symmetry of the system, the vibrational modes of the planar ZXY_2 molecule are all non-degenerate. In this case, it is possible to remove all the terms from H_1 into H_2'. The transformed Hamiltonian is

$$H_0'=H_0\,;\quad H_1'=0\,; \tag{8a}$$

$$\begin{aligned}H_2'=&-hc\{\tau_{xxxx}P_x^4+\tau_{yyyy}P_y^4+\tau_{zzzz}P_z^4+\tau_{xxyy}(P_x^2P_y^2+P_y^2P_x^2)+\tau_{yyzz}(P_y^2P_z^2+P_z^2P_y^2)\\&+\tau_{zzxx}(P_z^2P_x^2+P_x^2P_z^2)+\tau_{yzyz}(P_yP_z+P_zP_y)^2\}\\&+\left\{\left(\sum_{k=1}^{6}a_{kk}q_k^2\right)\frac{P_x^2}{I^{0\,2}_{xx}}+\left(\sum_{k=1}^{6}b_{kk}q_k^2\right)\frac{P_y^2}{I^{0\,2}_{yy}}+\left(\sum_{k=1}^{6}c_{kk}q_k^2\right)\frac{P_z^2}{I^{0\,2}_{zz}}\right\}+hcg_0+\frac{1}{2}\left(\frac{p_x^2}{I^0_{xx}}+\frac{p_y^2}{I^0_{yy}}+\frac{p_z^2}{I^0_{zz}}\right)\\&-hc\sum_{k=1}^{3}\frac{\beta^2_{kkk}}{\nu_k}\left[\frac{3p^2_{q_k}q_k^2}{\hbar^2}+1+\frac{3}{2}q_k^4\right]+hc\left\{\sum_{k=1}^{6}\gamma_{kkkk}q_k^4+\sum_{j=1}^{5}\sum_{k>j}^{6}(\gamma_{jjkk}-N_{jjkk})q_j^2q_k^2\right\}\\&-hc\left\{\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{\beta^2_{jjk}(1-\delta_{jk})}{2\nu_k(4\nu_j^2-\nu_k^2)}[(2\nu_j^2-\nu_k^2)q_j^4+4\nu_j\nu_kq_j^2q_k^2+2\nu_j^2q_j^2p^2_{q_j}/\hbar^2]\right\}\\&-hc\left\{\sum_{j=4}^{6}\sum_{k=1}^{3}\frac{\beta^2_{jjk}}{2\nu_k(4\nu_j^2-\nu_k^2)}[(2\nu_j^2-\nu_k^2)q_j^4+4\nu_j\nu_kq_j^2q_k^2+2\nu_j^2q_j^2p^2_{q_j}/\hbar^2]\right\},\end{aligned} \tag{8b}$$

where

$$\tau_{xxxx}=\frac{1}{8hcI^{04}_{xx}}\left(\frac{a_1^2}{\omega_1^2}+\frac{a_2^2}{\omega_2^2}+\frac{a_3^2}{\omega_3^2}\right),$$

$$\tau_{yyyy}=\frac{1}{8hcI^{04}_{yy}}\left(\frac{b_1^2}{\omega_1^2}+\frac{b_2^2}{\omega_2^2}+\frac{b_3^2}{\omega_3^2}\right),$$

$$\tau_{zzzz}=\frac{1}{8hcI^{04}_{zz}}\left(\frac{c_1^2}{\omega_1^2}+\frac{c_2^2}{\omega_2^2}+\frac{c_3^2}{\omega_3^2}\right),$$

$$\tau_{xxyy}=\frac{1}{8hc(I^0_{xx}I^0_{yy})^2}\left(\frac{a_1b_1}{\omega_1^2}+\frac{a_2b_2}{\omega_2^2}+\frac{a_3b_3}{\omega_3^2}\right),$$

$$\tau_{yyzz}=\frac{1}{8hc(I^0_{yy}I^0_{zz})^2}\left(\frac{b_1c_1}{\omega_1^2}+\frac{b_2c_2}{\omega_2^2}+\frac{b_3c_3}{\omega_3^2}\right),$$

$$\tau_{zzxx}=\frac{1}{8hc(I^0_{zz}I^0_{xx})^2}\left(\frac{c_1a_1}{\omega_1^2}+\frac{c_2a_2}{\omega_2^2}+\frac{c_3a_3}{\omega_3^2}\right),$$

$$\tau_{yzyz}=\frac{1}{8hc(I^0_{yy}I^0_{zz})^2}\left(\frac{e_4^2}{\omega_4^2}+\frac{e_5^2}{\omega_5^2}\right), \tag{9a}$$

[4] W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 895 (1939).

[5] S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941). In addition to the elements given in this table we need a term in S,

$$S=-a_{klm}\left\{\omega_k(\omega_k^2-\omega_l^2-\omega_m^2)\frac{p_kq_lq_m}{\hbar^2}+\omega_l(\omega_l^2-\omega_m^2-\omega_k^2)\frac{q_kp_lq_m}{\hbar^2}+\omega_m(\omega_m^2-\omega_k^2-\omega_l^2)\frac{q_kq_lp_m}{\hbar^2}-2\omega_k\omega_l\omega_mp_kp_lp_m/\hbar^2\right\}\Big/\hbar(\omega_k^2+\omega_l^4+\omega_m^4-2\omega_k^2\omega_l^2-2\omega_l^2\omega_m^2-2\omega_m^2\omega_k^2)$$

to remove the $a_{klm}q_kq_lq_m$ term from H_1.

$$\frac{a_{kk}}{hc}=\frac{\epsilon_{xk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{(1+2\delta_{jk})}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}}a_j\beta_{kkj}+\frac{1}{8\pi^2c^2\nu_k}\sum_{j=4}^{5}\frac{\zeta_{kj}^2(3\nu_k^2+\nu_j^2)}{\nu_k^2-\nu_j^2},\quad (k=1,2,3)$$

$$\frac{a_{kk}}{hc}=\frac{\epsilon_{xk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{a_j\beta_{kkj}}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}}+\frac{1}{8\pi^2c^2\nu_k}\sum_{j=1}^{3}\frac{\zeta_{jk}^2(3\nu_k^2+\nu_j^2)}{\nu_k^2-\nu_j^2},\quad (k=4,5)$$

$$\frac{a_{66}}{hc}=\frac{\epsilon_{x6}}{8\pi^2c^2\nu_6}+\sum_{j=1}^{3}\frac{a_j\beta_{66j}}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}},$$

$$\frac{b_{kk}}{hc}=\frac{\epsilon_{yk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{(1+2\delta_{jk})b_j\beta_{kkj}}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}}+\frac{\zeta_{k6}^2(3\nu_k^2+\nu_6^2)}{8\pi^2c^2\nu_k(\nu_k^2-\nu_6^2)},\quad (k=1,2,3)$$

$$\frac{b_{kk}}{hc}=\frac{\epsilon_{yk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}b_j\beta_{kkj}/2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}},\quad (k=4,5)$$

$$\frac{b_{66}}{hc}=\frac{\epsilon_{y6}}{8\pi^2c^2\nu_6}+\sum_{j=1}^{3}\frac{b_j\beta_{66j}}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}}+\frac{1}{8\pi^2c^2\nu_6}\sum_{j=1}^{3}\frac{\zeta_{j6}^2(3\nu_6^2+\nu_j^2)}{\nu_6^2-\nu_j^2},$$

$$\frac{c_{kk}}{hc}=\frac{\epsilon_{zk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{(1+2\delta_{jk})}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}}c_j\beta_{kkj},\quad (k=1,2,3)$$

$$\frac{c_{kk}}{hc}=\frac{\epsilon_{zk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{c_j\beta_{kkj}}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}}+\frac{\zeta_{k6}^2(3\nu_k^2+\nu_6^2)}{8\pi^2c^2\nu_k(\nu_k^2-\nu_6^2)},\quad (k=4,5)$$

$$\frac{c_{66}}{hc}=\frac{\epsilon_{z6}}{8\pi^2c^2\nu_6}+\sum_{j=1}^{3}\frac{c_j\beta_{66j}}{2h^{\frac{1}{2}}\omega_j^{\frac{1}{2}}}+\sum_{j=4}^{5}\frac{\zeta_{j6}^2(3\nu_6^2+\nu_j^2)}{8\pi^2c^2\nu_6(\nu_6^2-\nu_j^2)},\qquad (9b)$$

$$g_0=\frac{\beta_{123}^2\nu_1\nu_2\nu_3}{4D_{123}}+\sum_{k=1}^{3}\frac{\beta_{k45}^2\nu_k\nu_4\nu_5}{4D_{k45}}+\frac{h}{128\pi^2c}\sum_{k=1}^{3}\frac{\sigma_k^2}{\omega_k^2}+\frac{h}{16\pi^2c}\sum_{k=1}^{6}s_{kk};$$

$$D_{klm}=(\nu_k^4+\nu_l^4+\nu_m^4-2\nu_k^2\nu_l^2-2\nu_l^2\nu_m^2-2\nu_m^2\nu_k^2),\qquad (9c)$$

$$N_{kkjj}=\frac{3\beta_{kkk}\beta_{jjk}}{\nu_k}+\frac{3\beta_{jjj}\beta_{kkj}}{\nu_j}+\frac{\beta_{kkl}\beta_{jjl}}{\nu_l}+\frac{\beta_{123}^2\nu_l(\nu_l^2-\nu_k^2-\nu_j^2)}{2D_{123}},\quad (k=1,2,3;\ j=1,2,3;\ l=1,2,3)$$

$$N_{kk44}=\sum_{l=1}^{3}\frac{(1+2\delta_{kl})\beta_{kkl}\beta_{44l}}{\nu_l}+\frac{\beta_{k45}^2\nu_5(\nu_5^2-\nu_k^2-\nu_4^2)}{2D_{k45}},\quad (k=1,2,3)$$

$$N_{kk55}=\sum_{l=1}^{3}\frac{(1+2\delta_{kl})\beta_{kkl}\beta_{55l}}{\nu_l}+\frac{\beta_{k45}^2\nu_4(\nu_4^2-\nu_k^2-\nu_5^2)}{2D_{k45}},\quad (k=1,2,3)$$

$$N_{kk66}=\sum_{l=1}^{3}\frac{(1+2\delta_{kl})\beta_{kkl}\beta_{66l}}{\nu_l},\quad (k=1,2,3)$$

$$N_{4455}=\sum_{l=1}^{3}\left[\frac{\beta_{44l}\beta_{55l}}{\nu_l}+\frac{\beta_{l45}^2\nu_l(\nu_l^2-\nu_4^2-\nu_5^2)}{2D_{l45}}\right],$$

$$N_{kk66}=\sum_{l=1}^{3}\frac{\beta_{kkl}\beta_{66l}}{\nu_l}.\quad (k=4,5)\qquad (9d)$$

The general procedure is to set up the matrix of H' using as basic wave functions the harmonic oscillator functions $\psi_{V_i}(q_i)$ corresponding to vibrational quantum numbers V_i, and the symmetrical top functions $\psi_R^0(J, K, M)$. H' is diagonal in the vibrational quantum numbers (to the second order of approximation) and in the quantum numbers, J and M, and has only $(K|K)$, $(K|K\pm2)$,

$(K|K\pm4)$ elements in the quantum numbers $K=-J, -J+1, \cdots, J$. As is well known, the consequence of the latter fact is that the sub-matrix for a given vibrational state and J value can be reduced to a pair of sub-matrices corresponding to even and odd values of K, respectively. It was shown by Wilson[6] and in more detail by Shaffer and Nielsen[7] that by taking suitable linear combinations of the $\psi_R{}^0(J, K, M)$ each of the latter sub-matrices can be further reduced. The reduction indicated by Wilson can be effected also in the present case where $(K|K\pm4)$ elements are involved. Accordingly, we take as our set of basis functions

$$\begin{aligned}
\Psi_{gK}&=\prod_{i=1}^{6}\psi_{V_i}(q_i)\Lambda_K=\psi_V\frac{1}{\sqrt{2}}\{\psi_R{}^0(J,-K,M)+\psi_R{}^0(J,K,M)\}K>0,\\
\Psi_{g0}&=\sum_{i=1}^{6}\psi_{V_i}(q_i)\Lambda_0=\psi_V\psi_R{}^0(J,O,M),\\
\Psi_{uK}&=\prod_{i=1}^{6}\psi_{V_i}(q_i)\Phi_K=\psi_V\frac{1}{\sqrt{2}}\{\psi_R{}^0(J,-K,M)-\psi_R{}^0(J,K,M)\}K>0.
\end{aligned}\tag{10}$$

In terms of these we have

$$(\Psi_g{}^*|H'|\Psi_u)=(\Psi_u{}^*|H'|\Psi_g)=0\tag{11}$$

and the following non-vanishing elements:

$$\begin{aligned}
&\left.\begin{matrix}(V,\Lambda_K|V,\Lambda_K)\\(V,\Phi_K|V,\Phi_K)\end{matrix}\right\}=(R_0+R_2K^2+R_3K^4)\pm\delta_{K1}(R_4+2R_5)f\pm\delta_{K2}R_6f(f-2),\quad(K=0,1,\cdots,J)\\
&(V,\Lambda_0|V,\Lambda_2)=(V,\Lambda_2|V,\Lambda_0)=(R_4+4R_5)[2f(f-2)]^{\frac{1}{2}},\\
&\left.\begin{matrix}(V,\Lambda_K|V,\Lambda_{K+2})\\(V,\Phi_K|V,\Phi_{K+2})\end{matrix}\right\}=(R_4+R_5[K^2+(K+2)^2])[\{f-K(K+1)\}\{f-(K+1)(K+2)\}]^{\frac{1}{2}}\\
&\qquad\pm\delta_{K1}R_6f[(f-2)(f-6)]^{\frac{1}{2}},\quad(K>0)\\
&\left.\begin{matrix}(V,\Lambda_K|V,\Lambda_{K-2})\\(V,\Phi_K|V,\Phi_{K-2})\end{matrix}\right\}=(R_4+R_5[K^2+(K-2)^2])[\{f-K(K-1)\}\{f-(K-1)(K-2)\}]^{\frac{1}{2}}\\
&\qquad\pm\delta_{K3}R_6f[(f-2)(f-6)]^{\frac{1}{2}},\quad(K>2)\\
&(V,\Lambda_0|V,\Lambda_4)=(V,\Lambda_4|V,\Lambda_0)=R_6[2f(f-2)(f-6)(f-12)]^{\frac{1}{2}},\\
&\left.\begin{matrix}(V,\Lambda_K|V,\Lambda_{K\pm4})\\(V,\Phi_K|V,\Phi_{K\pm4})\end{matrix}\right\}=R_6[\{f-K(K\pm1)\}\{f-(K\pm1)(K\pm2)\}\{f-(K\pm2)(K\pm3)\}\\
&\qquad\times\{f-(K\pm3)(K\pm4)\}]^{\frac{1}{2}},\quad(K+4\geq5,\ K-4\geq1)
\end{aligned}\tag{12}$$

where $f=J(J+1)$, and

$$R_0=\frac{E_v}{hc}+J(J+1)\left\{\frac{X_e}{2}\left[1+2\sum_{k=1}^{6}\frac{a_{kk}}{I^0_{xx}}(V_k+\tfrac{1}{2})\right]+\frac{Y_e}{2}\left[1+2\sum_{k=1}^{6}\frac{b_{kk}}{I^0_{yy}}(V_k+\tfrac{1}{2})\right]\right.$$
$$\left.+\frac{h^4}{64\pi^4}(\tau_{xxxx}+\tau_{yyyy}-2\tau_{xxyy}-2\tau_{yzyz})\right\}-D_JJ^2(J+1)^2$$

with

$$X_e=\frac{h}{8\pi^2cI^0_{xx}};\quad Y_e=\frac{h}{8\pi^2cI^0_{yy}};\quad D_J=\frac{h^4}{128\pi^4}\{3(\tau_{xxxx}+\tau_{yyyy})+2\tau_{xxyy}\};$$

$$R_2=Z_e\left[1+2\sum_{k=1}^{6}\frac{c_{kk}}{I^0_{zz}}(V_k+\tfrac{1}{2})\right]-\frac{X_e}{2}\left[1+2\sum_{k=1}^{6}\frac{a_{kk}}{I^0_{xx}}(V_k+\tfrac{1}{2})\right]-\frac{Y_e}{2}\left[1+2\sum_{k=1}^{6}\frac{b_{kk}}{I^0_{yy}}(V_k+\tfrac{1}{2})\right]$$
$$-\frac{5h^4}{128\pi^4}(\tau_{xxxx}+\tau_{yyyy}-2\tau_{xxyy}-4\tau_{yzyz})-D_{JK}J(J+1)$$

[6] E. B. Wilson, Jr., J. Chem. Phys. **4**, 313 (1936).
[7] W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).

with

$$Z_e=\frac{h}{8\pi^2 cI^0_{zz}};\quad D_{JK}=\frac{h^4}{8\pi^4}\{\tau_{yzyz}+\tfrac{1}{2}(\tau_{yyzz}+\tau_{zzxx})-\tfrac{1}{4}\tau_{xxyy}-\tfrac{3}{8}(\tau_{xxxx}+\tau_{yyyy})\};$$

$$R_3=\frac{h^4}{8\pi^4}\{\tau_{yzyz}+\tfrac{1}{2}(\tau_{yyzz}+\tau_{zzxx})-\tfrac{1}{8}\tau_{xxyy}-\tfrac{1}{2}\tau_{zzzz}-\tfrac{3}{16}(\tau_{xxxx}+\tau_{yyyy})\};$$

$$R_4=\frac{X_e}{4}\left[1+2\sum_{k=1}^{6}\frac{a_{kk}}{I^0_{xx}}(V_k+\tfrac{1}{2})\right]-\frac{Y_e}{4}\left[1+2\sum_{k=1}^{6}\frac{b_{kk}}{I^0_{yy}}(V_k+\tfrac{1}{2})\right]-\frac{5h^4}{64\pi^4}\tau_{yzyz}-\frac{h^4}{64\pi^4}(\tau_{zzzz}-\tau_{yyyy})\bar{J}(J+1);$$

$$R_5=\frac{h^4}{128\pi^4}\{(\tau_{xxxx}-\tau_{yyyy})-2\tau_{zzxx}+2\tau_{yyzz}+4\tau_{yzyz}\};$$

$$R_6=\frac{h^4}{128\pi^4}\{\tau_{xxyy}-\tfrac{1}{2}(\tau_{xxxx}+\tau_{yyyy})\}. \tag{13}$$

The vibrational term in R_0 is defined by

$$\frac{E_v}{hc}=G_0+\sum_{k=1}^{6}(V_k+\tfrac{1}{2})\nu_k+\sum_{k=1}^{6}G_{kk}(V_k+\tfrac{1}{2})^2+\sum_{k=1}^{5}\sum_{j>k}^{6}G_{kj}(V_k+\tfrac{1}{2})(V_j+\tfrac{1}{2}), \tag{14}$$

where

$$G_0=g_0-\frac{7}{16}\sum_{k=1}^{3}\frac{\beta^2_{kkk}}{\nu_k}+\frac{3}{8}\sum_{k=1}^{6}\gamma_{kkkk}+\frac{3}{16}\left[\frac{\beta^2_{112}\nu_2}{4\nu_1^2-\nu_2^2}+\frac{\beta^2_{113}\nu_3^2}{4\nu_1^2-\nu_3^2}+\frac{\beta^2_{221}\nu_1}{4\nu_2^2-\nu_1^2}+\frac{\beta^2_{223}\nu_3}{4\nu_2^2-\nu_3^2}+\frac{\beta^2_{331}\nu_1}{4\nu_3^2-\nu_1^2}\right.$$

$$\left.+\frac{\beta^2_{332}\nu_2}{4\nu_3^2-\nu_2^2}+\sum_{k=1}^{3}\sum_{j=4}^{6}\frac{\beta^2_{jjk}\nu_k}{4\nu_j^2-\nu_k^2}\right]-\frac{X_e}{2}\sum_{k=1}^{3}(\zeta^2_{k4}+\zeta^2_{k5})-\frac{Y_e}{2}\sum_{k=1}^{3}\zeta^2_{k6}-\frac{Z_e}{2}(\zeta^2_{46}+\zeta^2_{56});$$

$$G_{kk}=\frac{3}{2}\gamma_{kkkk}-\frac{15}{4}\frac{\beta^2_{kkk}}{\nu_k}-\sum_{l=1}^{3}(1-\delta_{kl})\frac{(8\nu_k^2-3\nu_l^2)}{4\nu_l(4\nu_k^2-\nu_l^2)}\beta^2_{kkl};\quad (k=1,2,3)$$

$$G_{kk}=\frac{3}{2}\gamma_{kkkk}-\sum_{j=1}^{3}\frac{(8\nu_k^2-3\nu_j^2)}{4\nu_j(4\nu_k^2-\nu_j^2)}\beta^2_{kkj};\quad (k=4,5,6)$$

$$G_{jk}=\gamma_{jjkk}-N_{jjkk}-2\left[\frac{\beta^2_{jjk}\nu_j}{4\nu_j^2-\nu_k^2}+\frac{\beta^2_{kkj}\nu_k}{4\nu_k^2-\nu_j^2}\right];\quad (k,j=1,2,3)$$

$$G_{jk}=\gamma_{jjkk}-N_{jjkk}-\frac{2\beta^2_{kkj}\nu_k}{4\nu_k^2-\nu_j^2}+g_k\zeta^2_{jk}\left(\frac{\nu_j}{\nu_k}+\frac{\nu_k}{\nu_j}\right);\quad (j=1,2,3;\ k=4,5)$$

$$g_4=X_e;\quad g_5=Y_e;\quad g_6=Z_e.$$

$$G_{45}=\gamma_{4455}-N_{4455};$$

$$G_{k6}=\gamma_{kk66}-N_{kk66}+Z_e\zeta^2_{k6}\left(\frac{\nu_k}{\nu_6}+\frac{\nu_6}{\nu_k}\right);\quad (k=4,5). \tag{15}$$

The energies (in term value form) are the roots of the secular equations

$$|(\Psi^*_{g,K}|H'|\Psi_{g,K'})-\epsilon\delta_{KK'}|=0 \tag{16a}$$

and

$$|(\Psi^*_{u,K}|H'|\Psi_{u,K'})-\epsilon\delta_{KK'}|=0. \tag{16b}$$

It is evident from Eqs. (12) that (16a) and (16b) can each be factored into sub-determinants corresponding to even and odd values of K, respectively. Illustrations of this reduction are given by Shaffer and Nielsen.[7]

3. TREATMENT OF AN APPROXIMATE DEGENERACY

The planar ZXY_2 model is of particular interest in connection with the formaldehyde molecule. Ebers and Nielsen[8] have attributed the complex structure of its infra-red absorption spectrum in the 7.5–10μ region to a Coriolis type interaction between a pair of perpendicular vibrations,†† one of class B_1 and one of class B_2. Their point of view is that such interactions may become prominent when two fundamental frequencies happen to be nearly equal. Nielsen[3] has considered the effect for a restricted model,

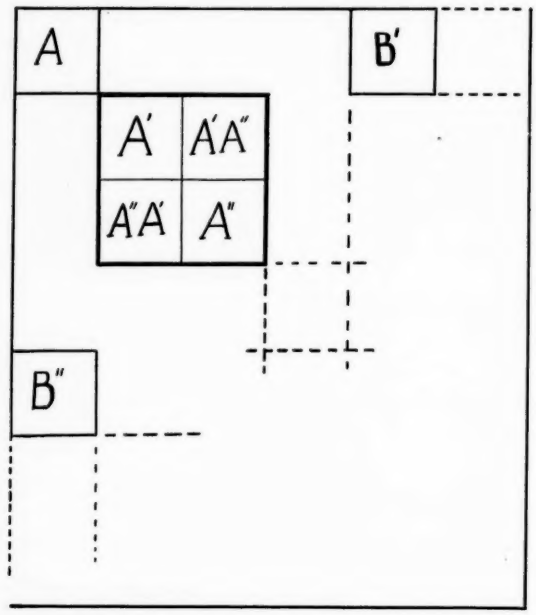


FIG. 1. Matrix of the transformed Hamiltonian when an approximate degeneracy exists between a pair of vibrational frequencies.

assuming formaldehyde to be a symmetrical top and neglecting the anharmonic terms in the potential energy. Wilson[6] has given a more general discussion for the asymmetrical top, but likewise neglected the anharmonic terms and other perturbing influences. He derived certain symmetry conditions which must be satisfied by the wave functions for the Coriolis perturbation to be significant. The states associated with the frequencies noted above satisfy these conditions. In the present section we present a more complete treatment for the lower energy states associated with these frequencies, taking into account all the first-order terms in the Hamiltonian. We denote the frequencies as ν_5 (class B_2) and ν_6 (class B_1), respectively.

The effect of the accidental degeneracy makes itself felt in applying the contact transformation to remove from H_1 the ζ_{56} term in the p_z component of the vibrational angular momentum (Eq. (4)). The element in the transformation function T required to remove this term is[5]

$$\zeta_{56}\frac{P_z}{I^0_{zz}}\left\{\frac{(\omega_5^2+\omega_6^2)q_5q_6+2\omega_5\omega_6 p_{q_5}p_{q_6}/h^2}{(\omega_5\omega_6)^{\frac{1}{2}}(\omega_6^2-\omega_5^2)}\right\}.$$

When the denominator becomes small, requirements as to orders of magnitude make such a term inadmissible. However, the contact transformation can be applied to remove all other terms in H_1, and we obtain in this case,

$$H_0'=H_0;$$

$$H_1'=-\frac{\zeta_{56}P_z}{I^0_{zz}}\left[\left(\frac{\nu_5}{\nu_6}\right)^{\frac{1}{2}}q_6p_{q_5}-\left(\frac{\nu_6}{\nu_5}\right)^{\frac{1}{2}}q_5p_{q_6}\right]. \quad (17)$$

H_2' retains the same form as in 8(b) except that we delete the ζ_{56} terms from the definitions of c_{55} and c_{66}. (18)

Using the set of wave functions defined in Eq. (10) as basis functions, we proceed as in Section 2 to set up the matrix of H'. As before, H' is diagonal in J and $V_1, \cdots, V_4$. The infinite sub-matrix for a given J value and set of vibrational quantum numbers $V_1, \cdots, V_4$ has the form shown in Fig. 1, corresponding to the totality of values of V_5 and V_6. The diagonal elements $A, A', A'', \cdots$ arise entirely from H_0' and H_2' and have precisely the same form as the sub-matrices of H' for given vibrational states developed in the preceding section. The definitions of $R_0, \cdots, R_6$ carry over completely except for the modification noted in (18). The non-diagonal elements are contributed entirely by H_1'. Elements $A'A''$ connect the pairs of states between which the approximate degeneracy exists, i.e., V_5, V_6 and $V_5\pm1$, $V_6\mp1$. Elements $B', B'', \cdots$ connect the states V_5, V_6 and $V_5\pm1$, $V_6\pm1$. The ratio of the orders of magnitude of the B' elements to the $A'A''$ elements is

[8] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. **5**, 822 (1937).

†† The abstract in reference 1 contains an error of statement concerning the pair of modes considered in this section.

[9] H. H. Nielsen, J. Chem. Phys. **5**, 818 (1937).

$(\nu_5-\nu_6)/(\nu_5+\nu_6)$, while the contribution of the elements B' to the energies of the lower states is of order of magnitude $(\nu_5-\nu_6)^2/\nu^3$. We are interested here in the ground state and the first excited states which give rise to the fundamental bands ν_5 and ν_6. To the first order of approximation, we may, therefore, neglect the elements B', B'', $\cdots$. Accordingly, the energies of the ground state are given by the developments in Section 2, setting $V_i=0$. For the first excited states we set up the matrix using the set of functions

$$\begin{aligned}
&\Psi_{ga}(K)=\Psi_g(V_5=1,\ V_6=0,\ K);\\
&\Psi_{gb}(K)=\Psi_g(V_5=0,\ V_6=1,\ K),\\
&\Psi_{ua}(K)=\Psi_u(V_5=1,\ V_6=0,\ K);\\
&\Psi_{ub}(K)=\Psi_u(V_5=0,\ V_6=1,\ K).
\end{aligned} \tag{19}$$

The elements of A' and A'', as noted above, are given by Eq. (12). Since

$$\begin{aligned}
&P_z\Lambda_k=-Kh\Phi_k;\quad P_z\Lambda_0=0;\\
&P_z\Phi_k=-Kh\Lambda_k,
\end{aligned} \tag{20}$$

the only non-vanishing elements of $A'A''$ and $A''A'$ are:

$$\begin{aligned}
(\Psi^*_{ga}|H_1'|\Psi_{ub})&=(\Psi^*_{ua}|H_1'|\Psi_{gb})=-(\Psi^*_{ub}|H_1'|\Psi_{ga})\\
&=-(\Psi_{gb}|H_1'|\Psi^*_{ua})=iR_1Khc;
\end{aligned} \tag{21}$$

where

$$R_1=\frac{\zeta_{56}h}{8\pi^2cI^0_{zz}}\left[\frac{\nu_5+\nu_6}{(\nu_5\nu_6)^{\frac{1}{2}}}\right]. \tag{21a}$$

From these results and the discussion in Section 2 of the elements entering into A' and A'' it is evident that the matrix can be reduced to two sub-matrices involving elements of Ψ_{ga} with Ψ_{ub} and Ψ_{gb} with Ψ_{ua}, respectively, and that each sub-matrix can be further reduced into a set of two according to odd and even values of K, respectively. The secular equations for $J=0, \cdots, 4$ are given below:

$J=0$

$$\epsilon=R_{0a};\quad \epsilon=R_{0b}. \tag{22}$$

$J=1$

$$\epsilon=R_{0a};\quad \epsilon=R_{0b}. \tag{23}$$

$$\begin{aligned}
&\epsilon^2-[R_{0a}+R_{2a}+R_{3a}+R_{0b}+R_{2b}+R_{3b}+\{R_{4a}-R_{4b}+2(R_{5a}-R_{5b})\}f]\epsilon\\
&\quad+[R_{0a}+R_{2a}+R_{3a}+(R_{4a}+2R_{5a})f][R_{0b}+R_{2b}+R_{3b}-(R_{4b}+2R_{5b})f]-R_1^2=0,
\end{aligned} \tag{24}$$

$$\begin{aligned}
&\epsilon^2-[R_{0a}+R_{2a}+R_{3a}+R_{0a}+R_{2b}+R_{3b}-\{R_{4a}-R_{4b}+2(R_{5a}-R_{5b})\}f]\epsilon\\
&\quad+[R_{0a}+R_{2a}+R_{3a}-(R_{4a}+2R_{5a})f][R_{0b}+R_{2b}+R_{3b}+(R_{4b}+2R_{5b})f]-R_1^2=0.
\end{aligned} \tag{25}$$

$J=2$

Equations (24) and (25), and

$$\begin{vmatrix}
R_{0a}-\epsilon & (R_{4a}+4R_{5a})[2f(f-2)]^{\frac{1}{2}} & 0 & \\
(R_{4a}+4R_{5a})[2f(f-2)]^{\frac{1}{2}} & R_{0a}+4R_{2a}+16R_{3a} & 2iR_1 & \\
 & \quad+R_{6a}f(f-2)-\epsilon & & \\
0 & -2iR_1 & R_{0b}+4R_{2b}+16R_{3b} & \\
 & & \quad-R_{6b}f(f-2)-\epsilon &
\end{vmatrix}=0. \tag{26}$$

Equations (26) with a and b interchanged. (27)

$J=3$

Equations (26) and (27), and

$$\begin{vmatrix}
R_{0a}+R_{2a}+R_{3a} & [R_{4a}+10R_{5a}+R_{6a}f] & iR_1 & 0 & \\
\quad+(R_{4a}+2R_{5a})f-\epsilon & \times\{(f-2)(f-6)\}^{\frac{1}{2}} & & & \\
[R_{4a}+10R_{5a}+R_{6a}f] & R_{0a}+9R_{2a} & 0 & 3iR_1 & \\
\times\{(f-2)(f-6)\}^{\frac{1}{2}} & \quad+81R_{3a}-\epsilon & & & \\
-iR_1 & 0 & R_{0b}+R_{2b}+R_{3b} & [R_{4b}+10R_{5b}-R_{6b}f] & \\
 & & -(R_{4b}+2R_{5b})f-\epsilon & \times\{(f-2)(f-6)\}^{\frac{1}{2}} & \\
0 & -3iR_1 & [R_{4b}+10R_{5b}-R_{6b}f] & R_{0b}+9R_{2b} & \\
 & & \times\{(f-2)(f-6)\}^{\frac{1}{2}} & \quad+81R_{3b}-\epsilon &
\end{vmatrix}=0. \tag{28}$$

Equation (28) with a and b interchanged. (29)

$J=4$

Equations (28) and (29), and

$$\begin{vmatrix} R_{0a}-\epsilon & (R_{4a}+2R_{5a})\times\{2f(f-2)\}^{\frac{1}{2}} & R_{6a}\{2f(f-2)\times(f-6)(f-12)\}^{\frac{1}{2}} & 0 & 0 \\ (R_{4a}+2R_{5a})\times\{2f(f-2)\}^{\frac{1}{2}} & R_{0a}+4R_{2a}+16R_{3a}+R_{6a}f(f-2)-\epsilon & (R_{4a}+20R_{5a})\times\{(f-6)(f-12)\}^{\frac{1}{2}} & 2iR_1 & 0 \\ R_{6a}\{2f(f-2)\times(f-6)(f-12)\}^{\frac{1}{2}} & (R_{4a}+20R_{5a})\times\{(f-6)(f-12)\}^{\frac{1}{2}} & R_{0a}+16R_{2a}+256R_{3a}-\epsilon & 0 & 4iR_1 \\ 0 & -2iR_1 & 0 & R_{0b}+4R_{2b}+16R_{3b}-R_{6b}f(f-2)-\epsilon & (R_{4b}+20R_{5b})\times\{(f-6)(f-12)\}^{\frac{1}{2}} \\ 0 & 0 & -4iR_1 & (R_{4b}+20R_{5b})\times\{(f-6)(f-12)\}^{\frac{1}{2}} & R_{0b}+16R_{2b}+256R_{3b}-\epsilon \end{vmatrix} = 0. \quad (30)$$

Equation (30) with a and b interchanged and R_1 replaced by $-R_1$. (31)

R_{ka} is the value of the constant R_k for the state $V_5=1$, $V_6=0$, and the given J-value; R_{kb} is the corresponding constant for the state $V_5=0$, $V_6=1$. The secular equations for the state $V_5=V_6=0$ can be obtained from the above by setting $R_1=0$ in each case and deleting the subscripts a and b. In the latter case only one of a pair of equations (e.g., (26) and (27)) need be used. The reduction of the secular equation, discussed in Section 2, effected by the use of the basis functions (10) is directly evident in the above equations.

The treatment above has given more than is required for a first-order approximation since the definitions of constants R_k contain terms contributed by H_2. These can be dropped from the final results with little difficulty. It should be noted that when the degeneracy is complete, i.e., $\nu_5-\nu_6=0$, the non-diagonal elements B', B'', $\cdots$ vanish and the secular Eqs. (22)–(31) give the energies to the second order of approximation.

The application of the results obtained in this paper to the analysis of the formaldehyde spectrum is in progress and will be reported in a later publication.

ACKNOWLEDGMENTS

The author takes pleasure in expressing his appreciation to Professor Harald H. Nielsen of The Ohio State University for many helpful discussions. He is particularly indebted to Professor Nielsen for having put his paper on the general molecule at the author's disposal before its publication.

The Near Ultraviolet Absorption Spectrum of Monodeuterobenzene

C. A. BECK, *Department of Physics, The Catholic University of America, Washington, D. C.*

AND

H. SPONER, *Department of Physics, Duke University, Durham, North Carolina*

The analysis of the ultraviolet absorption spectrum of monodeuterobenzene has been given. The spectrum is, as in benzene, a forbidden transition which is made allowed by the 603 vibration corresponding to the 606 ϵ^+_g benzene vibration. The 0,0 band is calculated to be 38,124, and it occurs with extreme weakness.

INTRODUCTION

THE near ultraviolet absorption spectrum of monodeuterobenzene lies in the same region as that of benzene.[1,2] This 2300–2650A region has been measured and the analysis of the bands made with the notation of light benzene.[3]

EXPERIMENTAL

The monodeuterobenzene was a sample prepared by Dr. F. A. Miller and Dr. R. C. Lord, Jr., of The Johns Hopkins University. It was introduced into the absorption cell in air and then the cell was pumped out, with two liquid-air traps arranged so as to avoid impurities from the pump. The spectra showed the presence of some light benzene, the percentage of which was roughly estimated from intensities to be about 15 percent. The light benzene lines can be seen clearly in Fig. 1, which represents the first weak group of both spectra. Figure 2 shows the gradual appearance of the monodeuterobenzene spectrum with pressure. All spectra were taken with the side arm of the absorption cell in a temperature bath, varying from 25°C to −70°C, while the main part of this quartz absorption cell of 50-cm length was at room temperature. A 5-meter concave aluminized grating, in the first order, with a dispersion of about 3.4A per mm was used. The same all-quartz discharge tube was used under the same conditions as in previous work.[1]

RESULTS

Table I contains the frequencies of the measured band-edges together with the intensities and assignments. The intensities are visual estimates from a plate with vapor pressure varying (in nine equal steps between the above temperatures), the number denoting that exposure at which the band is first visible. Broadness of bands, edge variance with vapor density, and differing microscope magnification contribute to the error in measurement. The main bands, given to tenths of cm^{-1} and measured under high magnification, are probably correct within one or two cm^{-1}. Other bands are somewhat less accurate.

[1] W. F. Radle and C. A. Beck, J. Chem. Phys. **8**, 507 (1940) (light benzene).
[2] H. Sponer, J. Chem. Phys. **8**, 705 (1940) (heavy benzene).
[3] H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, J. Chem. Phys. **7**, 207 (1939).

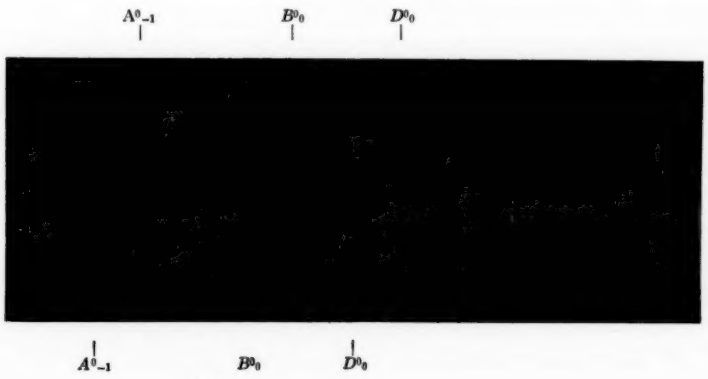


FIG. 1. Comparison of first weak group in light and monodeuterobenzene.

FIG. 2. Absorption spectrum of monodeuterobenzene at different pressures.

An effort was made to remove all light benzene lines from the table but some weak lines may have remained unnoticed. The table does not represent a complete list of all the other bands measured in monodeuterobenzene. Some 60 weak and very weak bands which were measured still less accurately are not included in Table I.

The spectrum resembles very much that of light benzene, as should be expected, but the appearance of the spectrograms is somewhat complicated by the simultaneous presence of C_6H_5D and C_6H_6.

ANALYSIS

The analysis of the monodeuterobenzene spectrum should be particularly interesting. Although the substitution of a light by a heavy hydrogen atom reduces formally the symmetry D_{6h} to C_{2v}, the electronic configuration of the benzene molecule remains unchanged. We would, therefore, expect the characteristic features of the benzene spectrum to show up unaltered in the monodeuterated compound. These features include the appearance of bands representing the 0–1 and 1–0 transitions (A^0_0 and B^0_0, respectively) of the 606 vibration which made the benzene spectrum allowed, and superimposed progressions of totally symmetrical vibrations and v–v transitions of non-totally symmetrical vibrations. The 0,0 band should not occur in a forbidden transition. However, since we do have the substitution, we actually have a very slight deviation from the benzene case which will result in a very slight perturbation. Although extremely small, it may be just sufficient to bring out the 0,0 band. We should then expect superimposed very faintly on this 0,0 band the features of the allowed C_{2v} transition.

The pure vibrational spectra of benzene and monodeuterobenzene should, contrary to the ultraviolet absorption spectra, be different from each other, one representing the selection rules for D_{6h} symmetry and the other one for C_{2v} symmetry because here the different masses are essential to the symmetry type. This has actually been found from Raman[4] and infra-red[5] investigations. Turning back to the ultraviolet absorption we then have the situation that vibrations resulting from C_{2v} symmetry will occur in the electronic spectrum which is caused by the molecule's electronic behavior almost completely according to D_{6h} symmetry. For example, the totally symmetrical carbon vibration of 981 cm^{-1} (992 in benzene) should represent all strong progressions. Other vibrations which are totally symmetrical only for C_{2v} and not for D_{6h} symmetry may occur, although with much less intensity. We expect especially carbon vibrations.

In analyzing the spectrum we then have a twofold task: to interpret the main part of the spectrum as coming from a forbidden transition $A_{1g} \rightarrow B_{2u}$ as in benzene with a vibrational structure analogous to that in benzene, but with additional probably fainter bands resulting from the vibrational C_{2v} symmetry of the monodeuterobenzene. Secondly, we must search for the possible appearance of a weak 0,0 transition, on which may be superimposed very faint bands with the characteristics of the allowed C_{2v} electronic transition. Finally, a comparison of this spectrum with the spectra of the monohalogenated benzenes should prove very interesting.

Proceeding now with the actual analysis we first note that the monodeuterobenzene has a great number of weak bands, possibly more so than the spectra of light and heavy benzene.

---

[4] A. Langseth and R. C. Lord, Danske Vidensk. Selskab. Math. Fys. Meddelel. **16**, No. 6 (1938); K. W. F. Kohlrausch, Phys. Zeits. **37**, 58 (1936); C. K. Ingold and collaborators, J. Chem. Soc. (1936), p. 925, p. 971.

[5] C. R. Bailey, J. B. Hale, C. K. Ingold, and J. N. Thompson, J. Chem. Soc. (1936), p. 931, p. 971.

This is in accordance with our theoretical expectations.

In analogy to benzene we interpret the band at 38,640.8 cm^{-1} as A^0_0. This band appears to consist mainly of one very strong component and the short edge of this was measured for rather low vapor pressure. Here, as in all cases, an effort was made to have a narrow region of light appear between the cross-hair and the short wave-length edge of the bands, which degrade to the red. The B^0_0 band probably consists of two components, and we have chosen the very strong component at 37,520.8 cm^{-1}. The component of longer wave-length which is very weak is not included in the table. A band at 37,529 could possibly belong to B^0_0, although A^0_0 has no corresponding band.

Just as in benzene, the difference between A^0_0 and B^0_0, namely, 1120 cm^{-1}, is the sum of the value of the same vibration in the ground and upper electronic states, which vibration makes the transition allowed. Similarly, the bands at 38,554.7 and 37,433.5 were interpreted as C^0_0 and D^0_0 according to 1–1 transitions of the same vibration superimposed on the A^0_0 and B^0_0 bands. The C^0_0 appears to be single while the D^0_0 appears somewhat like B^0_0. Choosing the strong component of D^0_0 (the very weak one is not included in the table) for the calculation of the drop in the discussed frequency, we obtain 87 cm^{-1}. Comparing this with the A^0_0 to C^0_0 distance, we obtain an average of 86.5. This together with the 1120 as the sum of the frequencies yields 603.2 cm^{-1} for the lower state and 516.7 cm^{-1} for the upper state of this particular vibration. We will use 603 and 517 as values, which gives 86 cm^{-1} for their difference. The 603 cm^{-1} compares well with the Raman[4] effect where 602 cm^{-1} has been observed. A difference of 88 cm^{-1} occurs in light benzene,[6] while it decreases to 82 cm^{-1} in heavy benzene. The 0,0 band can then be computed as 38,124. A pair of very faint bands appears at 38,123/38,124.5, which we are inclined to identify with the 0,0 band. We assume that the occurrence of this band is caused by the very slight deviation from the D_{6h} symmetry, in agreement with the theoretical considerations. No such band was observed in heavy benzene and its occurrence was very doubtful in light benzene. We estimate very roughly that the 0,0 band is about 10^3 times weaker than the A^0_0.

The 603 frequency which makes the transition allowed represents in benzene an ϵ^+_g vibration (value 606 cm^{-1}). In monodeuterobenzene, this splits into a β_1 and α_1 vibration, the first one being non-totally symmetrical, and the second one being totally symmetrical. As follows from the motion during this vibration, the β_1 keeps about the same value as the 606 vibration in benzene, whereas the α_1 is diminished in value. This effect is very pronounced if the substituent is of a heavy mass as in the halogenated benzenes (e.g., in C_6H_5Cl the β_1 is 611 and the α_1 is 416). It seems that in the A^0_0 and B^0_0 we observe mainly the non-totally symmetrical component. The totally symmetrical α_1 component is known from the Raman effect to be 598.5. It could occur according to the vibrational symmetries, also, although very faintly, superimposed on the 0,0 band. Because of the closeness of the values of the α_1 and β_1, the observance of the α_1 might be difficult, but a comparison between the corresponding bands of the three compounds shows that the bands in all three cases are so very much alike, that one may conclude from this that the α_1 component does not show up with appreciable intensity.

The totally symmetrical carbon vibration in the upper state which was 923 in light benzene and 879 in heavy benzene causes in monodeuterobenzene progressions with separations of 920 cm^{-1}. The first member is at 39,561 of which the violet edge was taken for the measurement. Corresponding progressions appear superimposed on B^0_0, C^0_0, and D^0_0 as can be seen from Table I. The vibration appears superimposed on these as well as on bands not yet mentioned. Since we interpreted the occurrence of the very weak 0,0 band as being caused by a very slight perturbation of the D_{6h} symmetry, we might expect bands of about the same very weak intensity resulting from excitations of the 920 vibration superimposed on the 0,0 vibration. There is indeed an indication of such a band at the right position. Of course there is always a possibility of explaining very weak bands by high Boltzmann factors, so that it is safer not to give any definite explanations of such bands.

[6] A difference of 86 cm^{-1} has been reported in reference 3, but later measurements suggest 88 cm^{-1} as best value; see also the last paragraph of this article.

TABLE I.

6	42116	$A'^0_1 = A'^0_0 + 920$
	42108	
7 L ?	42087	
6	41770	
	41427	
6*br*	41408	$A^0_3 = A^0_0 + 3\times920$ E^0_2 ?
7*br*	41393	
6	41205	
7	41196	$A'^0_0 = A^0_0 + 2555$
6 L ?	41164	
6*br*	41111	$C'^0_0 = C^0_0 + 2555$
6*br*	41083	
6*br*	41040	$A'^1_0 = A'^0_0 - 160$
6	40998	$B'^0_1 = B'^0_0 + 920$
6	40986	
6	40949	$C'^1_0 = C'^0_0 - 160$
6	40918	
5	40836	$B'^1_1 = B'^1_0 + 920$
6	40729	
6	40718	
6	40597	
7	40520.6	
7	40506.6	
8	40489.6	$E^0_1 = E^0_0 + 920$
8	40480.7	$A^0_2 = A^0_0 + 2\times920$
8	40472.5	
br	40390	$C^0_2 = C^0_0 + 2\times920$?
6 L ?	40373	
6	40340	$E^1_1 = E^1_0 + 920$? $K^0_2 = K^0_0 + 2\times920$
6	40322	
6*br*	40311	$A^1_2 = A^1_0 - 160$
6	40288	
6 L ?	40252	sup. $M^0_2 = M^0_0 + 2\times920$
5 L ?	40108	
7	40077	$B'^0_0 = B^0_0 + 2555$
6	40039	$G^0_1 = G^0_0 + 920$
5	40027	
7	40019	
6 L ?	40011	
5	39964	
5*br*	39917	$B'^1_0 = B'^0_0 - 160$
5	39894	
4	39878	$G^1_1 = G^0_1 + 920$
5	39867	
7	39808.0	
3	39788	
6	39743	
5	39675	
5*br*	39650	
7	39622	
7	39595.7	$A^0_0 + 955$?; 0,0+1472
	39592	
8	39581.3	$E^0_0 = 0,0 + 1458$
8	39571	0,0+1448
9	39561.1	$A^0_1 = A^0_0 + 920$
9	39552.7	
7	39473	$C^0_1 = C^0_0 + 920$
7	39466	
5	39437	39596−160
8	39419.6	$E^0_1 = E^0_0 - 160$
7	39401.4	$A^1_1 = A^0_1 - 160$
7	39392.6	
7	39364	$B^0_2 = B^0_0 + 2\times920$?
6	39343	
L	39331	sup. $M^0_1 = M^0_0 + 920$
	(39307)	$C^1_1 = C^0_1 - 160$?
6 L ?	39288	
6 L ?	39271	$D^0_2 = D^0_0 + 2\times920$
6 L ?	39263	$E^2_0 = E^0_0 - 2\times160$?
6 L ?	39256	
6	39241	$A^2_1 = A^2_0 + 920$
6	39228	
6	39221	
7	39116.7	$G^0_0 = A^0_0 + 2\times240$
6	39090.6	
w	39077	0,0+953
5	39068	
6	39059	
5	39022	
4	38963	
6	38958	$G^1_0 = G^0_0 - 160$
6	38938	
4	38913	
4	38891	
4*br*	38869	
4	38799	$G^2_0 = G^0_0 - 2\times160$
4	38733	
4	38688	
10	38640.8	$A^0_0 = 0,0 + 517$
7	38598	
6	38583	
8	38554.7	$C^0_0 = A^0_0 - 86$
7	38504.1	$K^0_0 = A^0_0 - 136$
5	38496	
8	38487.8	
8	38480.1	$A^1_0 = A^0_0 - 160$
7	38443.0	$B^0_1 = B^0_0 + 920$
6	38433.7	
7	38421.8	
7	38413.2	$M^0_0 = A^0_0 - 227$
6	38399	
7*br*	38395	$C^1_0 = C^0_0 - 160$
7	38374.5	
5 L ?	38352	$D^0_1 = D^0_0 + 920$
6 L ?	38343	$K^1_0 = K^0_0 - 160$
7	38335	
7	38326.8	
7	38320.8	$A^2_0 = A^0_0 + 2\times160$
7	38300.8	$L^0_1 = L^0_0 + 912$? $O^0_0 = A^0_0 - 338$
6 L ?	38284	
5	38275	$B^1_1 = B^1_0 + 920$
5	38256	$M^1_0 = M^0_0 - 160$
5*br*	38235	$C^2_0 = C^0_0 - 2\times160$
5	38227	
5	38215	$N^0_1 = N^0_0 + 920$
5	38210	
5	38196	
5	38183	$D^1_1 = D^0_1 - 160$; K^2_0 ?
5	38174	
5	38165	
w	38161	$A^3_0 = A^0_0 - 3\times160$
4	38156	
4	38142	$O^1_0 = O^0_0 - 160$
4	38130	
v.w.	38125	
	38123	0,0
	38118	$B^2_1 = B^2_0 + 920$
5	38114	
3	38108	$P^0_1 = P^0_0 + 920$
5*br*	38059	
4	38036	
2	38020	
3	38013	
4	38006	
4	37997	$A^4_0 = A^0_0 - 4\times160$
4	37982	$O^2_0 = O^0_0 - 2\times160$
2	37975	
4	37971	

TABLE I.—*Continued.*

3	37969	
4	37961	$H^0=0,0-160$?
4	37948	
2*br*	37914	
4	37896	$0,0-227$
2	37884	
2	37860	
2	37851	
2	37844	
3	37828	
3*br*	37820	
3	37801	$H^1=H^0-160$
3	37796	
3	37788	
3	37767	
3	37739	
3	37700	
2	37677	
2*br*	37668	
6	37659	$A^0_{-1}=A^0_0-981$
3	37636	
4	37630	
2	37604	
4	37578	
2*br*	37564	
5	37529	
7	37520	$B^0_0=0,0-603$
2	37454	
2	37442	
6	37433.5	$D^0_0=B^0_0-87$
4	37387	$L^0_0=B^0_0-134$
1	37381	
1	37375	
6	37367.8	
6	37360.7	$B^1_0=B^0_0-160$
4	37346	$D'=D^0_0-87$
4	37328	
4	37295	$N^0_0=B^0_0-226$
4	37280	
4	37275	$D^1_0=D^0_0-160$
3	37270	
4	37256	
w	37226	$L^1_0=L^0_0-160$
4	37207	
4	37201	$B^2_0=B^0_0-2\times160$
4	37185	$P^0_0=B^0_0-338$
3	37134	$N^1_0=N^0_0-160$
2	37119	
w	37046	
w	37041	$B^3_0=B^0_0-3\times160$
1*w*	37026	$P^1_0=P^0_0-160$

L means light benzene.

The 1008 vibration which is a β_{1u} in benzene and becomes totally symmetrical in monodeuterobenzene may be found to occur extremely weakly, if at all, superimposed on the A^0_0 and B^0_0 bands. It also, just as the 920 vibration, may occur in connection with the 0,0 band. From a careful search of the spectrum and a rough estimate of the percentual drop of this vibration we conclude that bands in the region of 39,590 may be associated with the superposition of this vibration on A^0_0, particularly the one at 39,595. This would give a frequency value of 955 cm^{-1} in the upper state. The band might, however, have another explanation or might represent the superposition of two different transitions. A faint band may be ascribed to a twofold excitation of 955 cm^{-1}. However, no definite evidence could be found for the occurrence of 955 superimposed on the B^0_0, which may be expected from the foregoing. A very weak band at 39,077 fits the assignment of 0,0+953.

The 160 progression of light benzene seems to occur unaltered in value in monodeuterobenzene. The appearance of the bands, however, is different. While in light benzene the B^1_0 has the same appearance as the B^0_0 (namely, a strong red component and a faint violet companion not quite 6 cm^{-1} apart) and the A^1_0 has two components of about equal intensity 4 cm^{-1} apart, in monodeuterobenzene there appear always two bands of about the same intensity, about 8 cm^{-1} apart from each other. It is quite possible that this doublet character of the 160 series comes from a splitting of the corresponding degenerate ϵ^+_u vibration in benzene, although one might expect that such a splitting would probably produce more diffuse bands on account of the overlapping of the components.

The *H* series, which in light benzene owes its existence to an excitation of an ϵ^+_u vibration in both the ground and excited states, occurs also in the spectrum of monodeuterobenzene, as can be seen in Table I. So does the *G* series which is an example of a 0–2 transition of this ϵ^+_u vibration superimposed on A^0_0.

The bands at 39,571 and 39,581 resemble bands in light benzene at 39,561 and 39,569 which have been called the first member of an *E* series arising from the excitation of the other ϵ^+_g vibration of 1596 cm^{-1} in the ground state. There appear in heavy benzene two bands at 39,693 and 39,706 which were taken as the first member of a similar *E* series, but it was pointed out that the larger distance of 13 cm^{-1} and particularly the larger drop of the ϵ^+_g vibration in heavy benzene made the explanation somewhat doubtful. In

TABLE II. The positions of the 0,0, A^0_0, and B^0_0 transitions for C_6H_6, C_6H_5D, and C_6D_6.

	C_6H_6	C_6H_5D	C_6D_6
0,0	38,090(calc.)	38,123.8	38,292(calc.)
A^0_0	38,610	38,641	38,790
B^0_0	37,482	37,521	37,712

monodeuterobenzene the bands are 10 cm^{-1} apart and the drop would be between those in the other two benzenes, but nearer to light benzene. The comparison of the E bands in all three benzenes makes the proposed explanation still seem to be the best, although it is not certain. We have bracketed the bands in the table but it is quite possible that only one of them qualifies for the proposed explanation. If we accept it for one or both bands we should expect, just as for the 606 vibration, a splitting of the 1596 into a totally symmetrical α_1 and a non-totally symmetrical β_1 component which give rise to a more complicated appearance of the E bands in the mono-compound. It is not probable that such a splitting occurs; there are two bands at 39,539 and 39,553 which fall in the A^0_1 region and might be taken as the pair belonging to the second component, but since we could not detect any indication of a splitting in the A and B bands, we hesitate to assume it for the E bands. We have not found any conclusive evidence for the occurrence of the totally symmetrical component of 1594 in the ground state and that of the non-totally symmetrical component of 1576 is very uncertain because it would coincide with B^0_{-1}.

Bands at 38,413/422 and 37,295 can be considered analogous to the bands M^0_0 and N^0_0 in heavy benzene. The separation of the M^0_0 and N^0_0 from the A^0_0 and B^0_0 was 202 cm^{-1} in heavy, 263 cm^{-1} in light benzene, and is 227 in monodeuterobenzene. The origin of these bands has been discussed previously[2] and it was pointed out that the occurrence of bands displaced by 207 and 263, respectively, from the 0,0 bands may indicate a square combination of symmetry ϵ^+_g for these bands. In monodeuterobenzene there occurs correspondingly a band displaced from the 0,0 band by 227 cm^{-1} toward longer waves, namely at 37,896 cm^{-1}. If we take this fact as support of the above-mentioned proposition and if, from intensity considerations and in analogy to the benzenes, we estimate the Boltmann factor of M^0_0 as being of the same magnitude as that of D^1_0, we may conclude that H vibrations of about 700–800 cm^{-1} are involved in these bands. The ϵ^-_g and ϵ^+_u vibrations were proposed previously as possibilities. No further decision, even with our additional data, can be given, however. The 920 progression and the difference of 160 appear superimposed on both the M^0_0 and N^0_0 bands.

In heavy benzene the letters K^0_0 and L^0_0 were assigned to bands which appear midway between C^0_0 and A^1_0, and D^0_0 and B^1_0, respectively. Their distances from C^0_0 and D^0_0 were 113 cm^{-1}. Light benzene showed no analogous bands of comparable intensity. In monodeuterobenzene we have found bands displaced from C^0_0 and D^0_0 by 135 cm^{-1} to the red. Their intensity is definitely smaller than that of the corresponding heavy benzene bands. It seems obvious that the bands represent 1–1 transitions but we are not able to assign them to a definite vibration. The superimposed 920 and 160 progressions do not stand out clearly because of some overlapping.

The totally symmetrical H vibration which was found to be 2565 cm^{-1} in the upper state of C_6H_6 obviously occurs also in monodeuterobenzene in the band at 41,196 with a value of 2555 cm^{-1}. It also occurs superimposed on B^0_0 and C^0_0. It is not possible to identify the totally symmetrical D vibration. The band in which it could occur in the ground state must be too weak for detection and as for the upper state there are too many bands which could be explained with the help of this vibration.

Finally, a few words may be said about the fine structure of the bands. As in the benzenes many bands appear to be double-headed. (The doublet character of the 160 series has probably a different cause and has been mentioned before.) We have taken here for the calculations the strong head. For the A^0_0 and C^0_0 bands this is the only measured edge, as also for B^0_0 and D^0_0. In the 920 progression of the A bands it is always the violet head if the two adjacent bands (for example, A^0_1, 39,553 and 39,561) constitute one band. The 920 progression of the B bands looks single. In this way our scheme of differences and frequency values was obtained. It is very

doubtful whether the faint companions on the violet side of the B^0_0 and D^0_0, 37,529 and 37,442, respectively, really are parts of these bands. We are inclined to believe that they are not, and we would like in this connection to take this question up again for the light benzene.

For C_6H_6 it had been tentatively suggested[3] to consider the corresponding strong red and weak violet bands of B^0_0, D^0_0, C^0_0 as R and Q branches of one band. The single nature of A^0_0 was explained by assuming that the strong absorption masked the structure and that the separation of 6 cm^{-1} found in the other bands between the R and Q bands, must be subtracted from the measured A^0_0 edge to obtain consistent numerical relations. The calculations were based on the measured value of 38,614.7 cm^{-1} of A^0_0. Since then it has been found in heavy benzene that a consistent scheme of relations and frequency values could be obtained by using always the strong edges and the present investigation yields the same result for monodeuterobenzene. Moreover, a remeasuring of the benzene bands changed the value of 38,614.7 for A^0_0 to 38,610.7 cm^{-1} so that the formerly obtained numerical relations do not come out consistently any more. This means that the difference between the values of the 606 ϵ^+_g vibration in the ground and excited states as calculated from the distance $A^0_0-B^0_0$ and from the known Raman value of 606 does not agree any more so closely with the distances $A^0_0-C^0_0$ or $B^0_0-D^0_0$. In fact, this close agreement is gone whether we subtract 6 cm^{-1} or not. Measurements of the bands with high dispersion* seem also to furnish doubt that the previous procedure of subtracting 6 cm^{-1} from the A^0_0 edge when making calculations is valid.

From the remeasured bands the 86 cm^{-1} difference becomes rather 88 cm^{-1}. The present small discrepancies would disappear if the value of the ϵ^+_g vibration in question were 608 instead of 606 cm^{-1}. The Raman frequency of 606 seems, however, well established. Another possibility is that the A^0_0 is still 2 cm^{-1} too high, although we feel this is a remote possibility only. It is, of course, always difficult to make sure that the edges of the bands are measured at a comparable "appearance pressure." With increasing pressure the bands broaden and the edges move a little toward the violet. Finally it is also possible that a slightly different structure of A^0_0 and B^0_0 could account for the deviations. Only from measurements with high dispersion may further information be expected.

---

* We are deeply indebted to Dr. Mark Fred and Dr. Anthony Turkevich for sending us enlargements of the A^0_0 and B^0_0 bands taken under very high dispersion.

Entropy of the Monomeric Forms of Formic Acid and Acetic Acid

J. O. HALFORD
Department of Chemistry, University of Michigan, Ann Arbor, Michigan
(Received May 19, 1942)

A recent measurement of the entropy of gaseous formic acid at its equilibrium vapor pressure is combined with vapor density data to give 60.0±0.3 as the entropy of the monomer at 25° and one atmosphere. The corresponding dimer entropy is 83.1±0.3 e.u. Pauling's residual entropy of R ln 2 per dimer weight for random orientation of hydrogen bonds in the crystal has been included in the above figures in order to allow a reasonable entropy for the torsional motion of the hydroxyl group in the monomer. The same correction has been applied to a previously published result for the acetic acid monomer to yield 70.1±1.0 as a revised value. It is highly probable that only a single significant potential minimum of undetermined breadth and depth occurs in the rotational cycle of the hydroxyl group.

FORMIC ACID

ACCURATE entropy values have recently been obtained by Stout and Fisher[1] for liquid and gaseous formic acid at 25° and the equilibrium vapor pressure. Their measurements include the redetermination of the vapor pressure (43.1 mm) and the heat of vaporization (4754±5 cal. for 46.026 g). It will be shown that their results can be combined with Coolidge's[2] vapor density data to give the entropy of the monomer as a hypothetical perfect gas with a probable error less than 0.3 e.u.

The calculation follows the same lines as the one recently made by the writer for acetic acid.[3] It is evident from the vapor density measurements, as Coolidge has stated, that at pressures below saturation, in the temperature range from 10° to 50°, the vapor is adequately described as a mixture of perfect gases in equilibrium according to the equation

$$(HCOOH)_2 = 2HCOOH. \qquad (1)$$

At higher temperatures and pressures the equilibrium quotient decreases with increasing pressure.

The equation

$$\log k = 24.6070 - 3754.9/T - 4.7034 \log T \qquad (2)$$

has been derived by the method of zero sums from fifty-four vapor density measurements made at temperatures from 10° to 80°. It was found that by including some data taken above 50°, the precision in determining the slope in the lower temperature range could be increased. This increase occurs at the expense of accuracy in the heat capacity term, which fortunately is of no importance to the present calculation. The method of least squares gives

$$\log k = 27.685 - 3904.3/T - 5.745 \log T. \qquad (2')$$

The sum of the squares of deviations, however, is about the same for Eq. (2) as for Eq. (2′). For the heat of dissociation of the dimer, the above equations lead to the expressions

$$\Delta H(\text{dis}) = 17{,}182 - 9.348\,T \qquad (3)$$

and

$$\Delta H(\text{dis}) = 17{,}866 - 11.399\,T \qquad (3')$$

and to the values 14,395 and 14,460 cal. at 25°. Further application of the least squares method with ΔCp arbitrarily set at zero yields 14,272 cal., which is below the limit of reasonable interpretation, since the curvature is obvious from the plotted function. By inspection, probable values lie well within the limits 14,400±120 cal.

The probable error of a single determination of log k may be taken as $(\Sigma v^2/n)^{\frac{1}{2}} = 0.0122$, where v is the deviation and n is the number of measurements. This quantity represents the largest reasonable estimate of the probable deviation of the mean from the true value. A more representative estimate would be lower, in the direction of $(\Sigma v^2/n^2)^{\frac{1}{2}}$, the quantity used for random deviations in n measurements of a single point. It seems safest here to use the larger probable error. Conversion to a probable error in the heat of dissociation is made by assuming that a plus or minus deviation of 0.0122 in log k might occur

[1] J. W. Stout and L. H. Fisher, J. Chem. Phys. **9**, 163 (1941).
[2] A. S. Coolidge, J. Am. Chem. Soc. **50**, 2173 (1928).
[3] J. O. Halford, J. Chem. Phys. **9**, 859 (1941).

with equal probability at either 10° or 80°, and applying the expression $\Delta H = -Rd \ln k/d(1/T)$. The result is a probable error of ±80 cal. In subsequent calculations, the rounded figure 14,400±100 cal. is used for the heat of dissociation.

From Eq. (2), $k_{298.1} = 2.361$ and the degree of dissociation $\alpha = (k/(k+4p))^{\frac{1}{2}} = 0.1162$. Individual heats of vaporization for the monomer and dimer may be obtained from the equations

$$\Delta H_1(46\text{ g}) = \frac{\Delta H(\text{vap})}{2} + \frac{1-\alpha}{2}\Delta H(\text{dis}) \quad (4)$$

and

$$\Delta H_2(92\text{ g}) = \Delta H(\text{vap}) - \alpha\Delta H(\text{dis}). \quad (5)$$

For the corresponding entropies of vaporization,

$$\Delta S_1(46\text{ g}) = \frac{\Delta H(\text{vap})}{2T} + \frac{1-\alpha}{2T}\Delta H(\text{dis}) + R \ln \frac{2\alpha p}{760(1+\alpha)} \quad (6)$$

and

$$\Delta S_2(92\text{ g}) = \frac{\Delta H(\text{vap})}{T} - \frac{\alpha\Delta H(\text{dis})}{T} + R \ln \frac{(1-\alpha)p}{760(1+\alpha)}, \quad (7)$$

where $\Delta H(\text{vap})$ and $\Delta H(\text{dis})$ apply to 92 g of the acid and p is the equilibrium vapor pressure.

Numerical substitution into Eqs. (6) and (7) gives 28.48 and 20.11 for the respective entropies of vaporization. By combination with the Stout and Fisher result, 30.82 e.u. per monomer weight of liquid, the entropies of the hypothetical perfect gases at 25° and one atmosphere are found to be

$$S_1 = 59.30 \quad \text{and} \quad S_2 = 81.75 \text{ (prelim.)}.$$

The sum of probable errors in S_1 introduced by the heats of vaporization and dissociation and by the pressure and the degree of dissociation is 0.3 e.u., and the combined probable error is 0.2 e.u. The probable error in S_2 is about the same, in spite of the double weight of acid.

Consideration may now be given to the question of residual entropy in the crystal, as predicted by Pauling.[4] For this purpose the entropy contributed by torsional motion of the hydroxyl group is found by subtracting the sum calculated for the remaining degrees of freedom from the monomer entropy. All angles between single bonds are assumed to have the tetrahedral value and interatomic distances are taken as C−H = 1.09, C=O = 1.24, C−O = 1.43 and O−H = 0.97A units. The mean of moment of inertia products for models with *cis*- and *trans*-orientation of the hydroxyl group, differing by only 0.1 in their contribution to the entropy, has been used. Frequencies of the normal vibrations are taken from Bonner and Hofstadter and from Herman and Williams[5] as 3570, 2940, 1221, 1190, 1111, 1075, and 658 cm^{-1}. There can be little doubt of the correctness of assigning the lowest frequency as a fundamental, and only this one must be accurate and correctly assigned for the present purpose.

The calculated monomer entropy, exclusive of the torsional motion, is 59.25 e.u., to be compared with 59.30 based upon the thermal and vapor density data. The contribution of the internal rotation or vibration is then $0.05 \pm 0.3 + S(\text{res})$, where $S(\text{res})$, the entropy at the absolute zero, may be zero, or, if Pauling's prediction is correct, $\frac{1}{2}R \ln 2 = 0.69$. From these figures the larger torsional entropy, 0.74±0.3 e.u., appears by far the more probable. This corresponds to a harmonic frequency range from 380 to 600 cm^{-1}, whereas the zero residual entropy would correspond to the range from 650 to 1150 cm^{-1}, which is less reasonable. The monomer and dimer entropies are therefore revised to

$$S_1 = 60.0 \pm 0.3 \quad \text{and} \quad S_2 = 83.1 \pm 0.3.$$

If the hydroxyl group is arbitrarily treated as a symmetrical rotator with a moment of inertia of 1.35×10^{-40} it will contribute in free rotation 4.45 units to the entropy at 25°, leading to a total free rotation entropy of 63.7. This treatment omits some small subtractions called for by Kassel's determinant.[6] It is easy to show, however, that the refinements of his interesting and ingenious procedure are numerically unimportant except for molecules of very low molecular weight.

The above calculations indicate that in formic acid an entropy deficiency of 3.7±0.3 units results from hindrance of the internal rotation.

ACETIC ACID

It is probable that acetic acid also has residual entropy at the absolute zero due to random

[4] L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).

[5] L. G. Bonner and R. Hofstadter, J. Chem. Phys. **6**, 53 (1938); R. C. Herman and V. Williams, J. Chem. Phys. **8**, 447 (1940).

[6] L. S. Kassel, J. Chem. Phys. **4**, 276 (1936).

orientation of hydrogen bonds. The value recently published by the writer should therefore be increased from 69.4 to 70.1 ($\pm$1.0) e.u. The decision is based entirely upon the more accurate formic acid calculation, since an unknown uncertainty in the entropy of liquid acetic acid makes it necessary to leave a relatively wide allowance for error. For this reason the residual entropy problem was not considered in connection with the original acetic acid calculation.

In addition, a revision of the estimated free rotation entropy is in order. The vibrational contribution was taken from the mechanically analogous acetone molecule, for which it had been assumed that rotation of the methyl groups is practically unhindered. A recent simultaneous consideration of acetic acid, acetone and isobutylene, in conference with Dr. R. H. Gillette, has led to the conclusion that the vibrational entropy of acetone and acetic acid should be about 1.2 units higher than originally assigned. This raises the free rotation value for acetic acid from 72.7 to 73.9, and leaves 3.8 units for the deficiency below the free rotation entropy. Of this quantity, by analogy with acetone, about 0.6 should be subtracted for the methyl group, leaving 3.2$\pm$1.0 for the hydroxyl group.

THE CARBOXYL GROUP

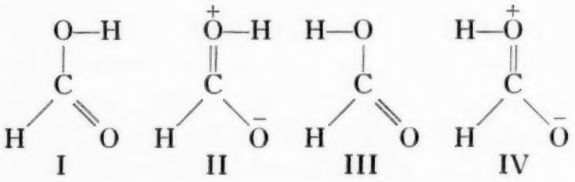
The estimated probable errors are large enough to obscure any difference between the entropy deficiencies calculated for the two acids. It is permissible to conclude that the deficiencies are large and roughly equal, and to add the suspicion that a greater hindrance to free rotation may occur in formic acid.

The above revision of the acetic acid entropy produces no appreciable change in the calculated entropy deficiency. Consequently the tentative explanation made in connection with the first calculation is still equally applicable. If hindrance of rotation was ascribed to a single sinusoidal potential valley covering one-third of the cycle, the large deficiency could occur with a potential barrier of approximately 3000 cal. For acetic acid this interpretation could only be called somewhat probable because of the rather large probable error assigned to the entropy deficiency.

The more accurate formic acid result permits a more objective consideration leading to the same type of description. There must be at least one important potential minimum to account for the large deficiency below free rotation (3.7$\pm$0.3 e.u.). From the shape of the molecule alone as many as three more minima are possible, but they are readily shown to be relatively unimportant. For this purpose it is convenient to consider the contribution of the torsional motion (0.75$\pm$0.3 e.u.) as an entropy of mixing $-R\Sigma X_i \ln X_i$ where X_i is the fraction of molecules to be found in the ith energy state, vibrational or rotational. If, for example, there were two states of approximately equal probability, the entropy would be $R \ln 2$, or 1.38. Still larger values would result from the occurrence of three comparable states, or from the subdivision of either or both of the two states just considered. If all the molecules were divided between two states, about 85 percent of them would be in the more populated one.

It is probable, then, that the one minimum description is at least qualitatively correct, since the occurrence of other important minima would cause distribution of the molecules over two or more comparable states and the resulting entropy would be much larger than the calculated value. The results, however, do not permit any specific conclusions about the height or effective width of the potential valley. The barrier will not be unusually high if the valley does not cover more than about one-third of the cycle.

A single configuration might be considerably stabilized by resonance of the arrangements I and II.



Formulas II and IV would produce potential minima corresponding to *cis-trans*-isomerism which would presumably favor II because of the attraction of the negatively charged oxygen atom for the proton. If, in addition, a repulsion between the hydrogen atoms occurred, IV would be still less stable relative to II, and the *trans*-minimum might be substantially eliminated. The configuration described in terms of the *cis*-forms I and II would then predominate over the alternative situation embraced by formulas III and IV.

Solvent Effects on the Kinetics of Ionic Reactions and the Choice of the Concentration Scale*

HUBERT G. DAVIS AND VICTOR K. LAMER
Department of Chemistry, Columbia University, New York, New York

(Received May 26, 1942)

The mole fraction scale gives simpler (i.e., more nearly linear) relations between the variables determining kinetics on changing solvents for the bromacetate-thiosulphate reaction than does the usual volume molar scale. The generality and basis of this finding is discussed from the viewpoint of Rabinowitch's cage model theory as well as from that of equilibrium theory. The quenching of fluorescence, which involves diffusion as a rate determining step, is a more nearly linear function of the fluidity when the data are expressed in mole fraction than in the volume molar scale. Experiments are in progress to determine, if possible, whether the cage model or a modified Smoluchowski diffusion treatment fits the facts better for low activation energy reactions like the quenching of fluorescence in solution.

1. INTRODUCTION

SELECTION of the proper concentration scale to be used in comparing either reaction rate or equilibrium constants becomes a problem of importance when the molecular volumes of the solvents differ considerably. For example two bimolecular rate constants which are equal on the mole fraction scale in methyl and in iso-amyl alcohol stand in a ratio of 1 to 3 when compared on a volume molar basis.

In calculating thermodynamic properties, it has been customary to employ the mole fraction scale, whereas in reaction kinetics the universal use of the volume molar scale has not been questioned until recently.[1,2]

It has been suggested that apparent anomalies in the effect of added sucrose and ethanol upon the rate in aqueous solution of the reaction[1,3-7]

$$S_2O_3^{=}+BrCH_2COO^{-}=Br^{-}+CH_2S_2O_3COO^{=}$$

can be eliminated by the conversion of the data from volume molar to mole fraction units.

In order to investigate this suggestion and to attempt to correlate residual and unexplained solvent effects, we have further studied the effect of solvent and of temperature upon this reaction. Data on the solubility of thallous chloride in solvents of differing molecular volume have been obtained for purposes of comparison.

Ions in Solution

Electrostatic theory, applied to a reaction in dilute solution between two ionic reactants A and B of charge Z that form a double-sphere critical complex, leads to the well-known rate equation[8,9]

$$\ln k=\ln k_{D=\infty}-\frac{Z_AZ_B\epsilon^2N_{Av}}{DRT}\cdot\frac{1}{r_A+r_B}+\frac{Z_AZ_B\epsilon^2N_{Av}}{DRT}\cdot\frac{\kappa}{1+\kappa a}, \quad (1)$$

where a is the Debye-Hückel first approximation parameter, r_A+r_B is the separation of the centers of charge in the critical complex, $\kappa=(8\pi\epsilon^2N_{Av}^2\mu/DRT1000)^{\frac{1}{2}}$ from the Debye-Hückel theory,[10] and the other symbols have their usual significance. Analogous equations have been developed from the Debye-Hückel theory for the constants of ionic equilibria. For the solubility of a strong binary electrolyte AB the expression is[9,11]

$$\ln S=\ln S_{D=\infty}-\frac{Z^2\epsilon^2N_{Av}}{2DRT}\left(\frac{1}{r_A}+\frac{1}{r_B}\right)+\frac{Z^2\epsilon^2N_{Av}}{2DRT}\cdot\frac{\kappa}{1+\kappa a}. \quad (2)$$

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

Constructed from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University by Hubert G. Davis in October, 1941.

[1] G. Scatchard, J. Chem. Phys. **7**, 657 (1939), discussion by LaMer, p. 662; Ann. N. Y. Acad. Sci. **39**, 341 (1940).

[2] R. P. Bell, Ann. Repts. on Progress of Chemistry **36**, 82 (1939).

[3] LaMer and Kamner, J. Am. Chem. Soc. **57**, 2662 (1935); **57**, 2669 (1935).

[4] Straup and Cohn, J. Am. Chem. Soc. **57**, 1794 (1935).

[5] Tomlinson, Dissertation, Columbia University, N. Y. (1939).

[6] V. K. LaMer, J. Frank. Inst. **225**, 709 (1938).

[7] Kappana, J. Ind. Chem. Soc. **6**, 419 (1929).

[8] Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).

[9] G. Scatchard, J. Am. Chem. Soc. **52**, 52 (1930); Chem. Rev. **10**, 229 (1932).

[10] Debye and Hückel, Physik. Zeits. **24**, 185 (1923).

[11] Ricci and Davis, J. Am. Chem. Soc. **62**, 407 (1940).

In such equations the logarithm of the constant, or the change in standard free energy of the equilibrium between reactants and critical complex, is expressed as the sum of three terms,[6] the first equal to the value at infinite dielectric constant and thus free of all electrostatic effects; the second, or self-potential term arising from the work of charging the ions in a medium of dielectric constant D; and the third expressing the effect of the ionic atmosphere at an ionic strength μ.

The third term of Eqs. (1) and (2) offers a simple method of extrapolation to infinite dilution ($\kappa=0$), by a suitable choice of the parameter a. When the simple Debye-Hückel theory cannot be applied, this term may be modified by use of the idea of ion-association,[12,13] but the extrapolation is often unsatisfactory.

Both Eqs. (1) and (2) predict that the plot of $\log k_{\kappa=0}$ or $\log S_{\kappa=0}$ *vs.* $1/D$ will be linear. The value of r_A+r_B or $1/r_A+1/r_B$ can be determined from the slope. Such a linear plot is often found, but there are serious objections to the literal interpretation of the self-potential term: the value of r_A+r_B is often either too large or too small for the physical model[14,15] and may even be negative; it is in general dependent on both temperature and solvent; the use of the macroscopic dielectric constant has long been considered questionable, since the orientation of the solvent dipoles in the field of the ions will make the effective dielectric constant lower.[16] The plot of $\log k_{\kappa=0}$ *vs.* $1/D$ is not always linear and indeed always shows curvature at sufficiently low dielectrics. Imperfect extrapolation to zero ionic strength is an important cause of such curvature, but there is reason to suspect that even when the extrapolation is valid, a linear plot may not always be obtained.

The Normalized Mole Fraction Rate Constant

Conversion of a second-order reaction rate constant k from volume-molar units, liters per mole, to mole fraction units, total moles per mole, requires multiplication by the factor, total moles per liter. If the mole fraction constant is divided by the total number of moles per liter in a standard solvent, a normalized constant, k^N, is obtained. This is proportional to the mole fraction constant, but becomes equal to the volume molar constant when the standard solvent is used.[1]

$$k^N = k\frac{\sum \text{Moles/liter}}{\sum (\text{Moles/liter})_{\text{standard}}}. \qquad (3)$$

Water at 4°, with 55.5 moles per liter, has been chosen as the standard solvent to which the data of this paper on the bromacetate-thiosulfate reaction have been referred.

Consider a reaction of the type

$$A+B\underset{k_2}{\overset{k_1}{\rightleftarrows}}X\xrightarrow{k_2}\text{Products},$$

where X denotes the critical complex. Let K_X be the equilibrium constant $(N_X/N_AN_B)(\gamma_X/\gamma_A\gamma_B)$ of the former equilibrium, N = mole fraction and γ = mole fraction activity coefficient, and let the rate determining step of the over-all reaction be the unimolecular decomposition of the critical complex:

$$-\frac{d[X]}{dt}=k_3[X]=k_3K_X\frac{N_AN_B}{N_X}\frac{\gamma_A\gamma_B}{\gamma_X}[X]. \qquad (4)$$

$$k=\text{Molar rate constant}=\frac{-d[X]/dt}{[A][B]}$$

$$=k_3K_X\frac{\gamma_A\gamma_B}{\gamma_X}\frac{N_A}{[A]}\frac{N_B}{[B]}\frac{[X]}{N_X}$$

$$=k_3K_X\frac{\gamma_A\gamma_B}{\gamma_X}\left(\sum\frac{\text{moles}}{\text{liter}}\right)^{(1-m)}, \qquad (5)$$

where $m=2$ is the total number of reactants. Generalizing the definition of K^N (Eq. (3)), we have

$$k^N=k\frac{\left(\sum\frac{\text{moles}}{\text{liter}}\right)^{(m-1)}_{\text{solvent}}}{\left(\sum\frac{\text{moles}}{\text{liter}}\right)^{(m-1)}_{\text{standard}}}$$

$$=k_3K_X\frac{\gamma_A\gamma_B}{\gamma_X\left(\sum\frac{\text{moles}}{\text{liter}}\right)^{(m-1)}_{\text{standard}}}. \qquad (6)$$

[12] Bjerrum, K. Danske Vidensk. Selskab, **7**, No. 9 (1926).
[13] Hogge and Garrett, J. Am. Chem. Soc. **63**, 1089 (1941).
[14] Amis and LaMer, J. Am. Chem. Soc. **61**, 905 (1939).
[15] Amis, J. Am. Chem. Soc. **63**, 1606 (1941).
[16] H. Frank, J. Am. Chem. Soc. **63**, 1789 (1941).

Since k_3 has the dimensions of frequency, we denote it by the symbol ν. If K_x is replaced by its thermodynamic equivalent, Eq. (5) becomes for a bimolecular reaction

$$k=\nu e^{-\Delta H_0^{\ddagger}/RT}e^{\Delta S_0^{\ddagger}/R}\frac{\gamma_A\gamma_B}{\gamma_X}\left(\Sigma\frac{\text{moles}}{\text{liter}}\right)^{-1}. \quad (7)$$

The corresponding Eyring absolute rate equation for a bimolecular reaction in solution is[17]

$$k=\frac{RT}{Nh}e^{-\Delta E_{exp}/RT}e^{\Delta S^{\ddagger}/R}\frac{\gamma_A\gamma_B}{\gamma_X}\left(\Sigma\frac{\text{moles}}{\text{liter}}\right)^{-1}, \quad (8)$$

where ΔE_{exp} or E_{act} is obtained from the slope of $\log k$ *vs* $1/T$ and where we have added the activity coefficient term and imply a mole fraction equilibrium constant K_x.

Using the "cage model" of a liquid, Rabinowitch[18,19] has developed an improved collision theory of bimolecular reaction rates in solution. His equation is

$$k=n\frac{N_{Av}}{N_0}\nu e^{-E_{act}/RT}\Big/\left(1+\frac{a^2\gamma_1}{4D_i}\nu e^{-E_{act}/RT}\right), \quad (9)$$

in which n is the coordination number (effective for reaction) of a reactant molecule, N_0 is the number of liquid lattice points per liter, a is the "lattice distance," D_i is an average diffusion coefficient of the reactants, ν is a frequency characteristic of the solvent, γ_1 is a factor accounting for the fact that a "jump" of molecule B may not destroy coordination with molecule A, and the other symbols have their usual significance.

Equation (9) shares with earlier collision equations based on gas kinetics the disadvantage of neglecting the entropy factor $\exp \Delta S^*/R$ arising from the internal degrees of freedom of the molecules concerned. It is nevertheless valuable because of the clear picture it gives of the significance of a "collision" and of the positional condition for reaction; namely, that two molecules must be in a state of coordination in order to react. Equation (9) also distinguishes clearly reactions with negligible energy of activation, and an observed dependence on viscosity from the commonly studied reactions with appreciable energy of activation and no observable dependence on viscosity. If E_{act} is small, the equation reduces to

$$k=4nN_{Av}D_i/N_0a^2\gamma_1 \quad (10)$$

and for larger values of E_{act}, to

$$k=\frac{nN_{Av}}{N_0}\nu e^{-E_{act}/RT}. \quad (11)$$

If N_0 is equal to the total number of all molecules per liter and if n remains constant, the simple Eq. (11) predicts that k^N will be independent of solvent.

As it stands, Eq. (11) is evidently incompatible with Eqs. (5), (7), and (8). Arbitrary insertion into Eq. (11) of the missing entropy and activity coefficient factors, which must be found in any acceptable equation, gives

$$k=n\frac{N_{Av}}{N_0}\nu e^{-E_{act}/RT}e^{\Delta S^{\ddagger}/R}\frac{\gamma_A\gamma_B}{\gamma_X}. \quad (12)$$

Comparison of Eqs. (12) and (7) clarifies the significance of the mole fraction rate equation in terms of collisions. If the total number of lattice positions per unit volume, N_0, were a constant independent of the solvent, Eq. (12) would be essentially the usual volume molar rate equation. When however rate constants in solvents of differing molecular volume are compared in mole fraction units, the tacit assumption is made that the total number of molecules per liter present, the total number of positions in the liquid lattice, and the effective number of lattice positions for the reactant molecules are equal to each other. With these assumptions, Eq. (12) becomes essentially identical with Eq. (7).

Temperature Coefficients of Ionic Reactions

The energy and entropy of activation of an ionic reaction, calculated in the usual way at constant solvent composition, are functions of dD/dT for the particular solvent used.[6,14,20,21] It

[17] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (The McGraw-Hill Book Company, New York, 1941), p. 199.

[18] Rabinowitch, Trans. Faraday Soc. **33**, 1225 (1937); Rabinowitch and Wood, *ibid.* **32**, 1381 (1936).

[19] Mark and Simha, Naturwiss. **25**, 833 (1937).

[20] Svirbely and Warner, J. Am. Chem. Soc. **57**, 1883 (1935).

[21] Warner, Ann. N. Y. Acad. Sci. **39**, 345 (1940).

has been pointed out that according to Eq. (1) the effect of electrostatic forces on the temperature coefficient may be removed by extrapolating log k to infinite dielectric constant, $1/D=0$. Thus values of the entropy, $\Delta S^{\ddagger}$, and energy, $\Delta E^{\ddagger}$, of activation may be obtained, which are independent of the ionic properties of the reactants. Consideration of Eq. (1) suggests that the value of the entropy of activation so obtained is equivalent[6,20,21] to the so-called isodielectric entropy of activation, $\Delta S^{\ddagger}_{\text{const } D}$ obtained by arbitrarily varying the composition of the solvent in such a manner as to maintain the dielectric constant independent of temperature.

Moreover, we note that by varying the solvent composition in such a way that the product DT is maintained constant, it is possible according to Eq. (1) to obtain a temperature coefficient and therefore an energy of activation, $\Delta E^{\ddagger}_{\text{const } DT}$ independent of the electrostatic terms and equal to $\Delta E^{\ddagger}_{D=\infty}$.

In this case it is not necessary to compare results at zero ionic strength, but only at constant concentration of reactants, provided that the rate constant is separable into three terms as in Eq. (1) and that the ionic atmosphere term involves D and T only as the product; this is true not only of Eq. (1) but of all equations derived from the Debye-Hückel postulates, such as those of Bjerrum[12] and of Gronwall, LaMer, and Sandved.[22]

When the temperature coefficient is measured with D held constant, the entire electrostatic effect is arbitrarily thrown into the energy of activation, $\Delta E^{\ddagger}_{\text{const } D}$. Likewise when the product DT is held constant the electrostatic effect is arbitrarily absorbed in the entropy term, $\Delta S^{\ddagger}_{\text{const } DT}$.

Equation (1) predicts that $\Delta S^{\ddagger}_{\text{const } D}$ and $\Delta E^{\ddagger}_{\text{const } DT}$ will be independent of dielectric constant and of solvent. Failure to find such an independence may be taken as indicative of the importance of solvent effects not accounted for by an equation derived from simple electrostatic postulates alone. In particular the consideration of $\Delta E^{\ddagger}_{\text{const } DT}$ may help to determine the relative importance of electrostatic and non-electrostatic effects even when a satisfactory extrapolation to zero ionic strength cannot be made. If $\Delta S^{\ddagger}_{\text{const } D}$ and $\Delta E^{\ddagger}_{\text{const } DT}$ really approximate closely the values for the reaction freed of electrostatic effects, they may be expected to be practically temperature independent.

[22] Gronwall, LaMer, and Sandved, Physik. Zeits. **29**, 558 (1928).

NEW EXPERIMENTS ON BROMACETATE-THIOSULFATE REACTION

A. Materials

Bromacetic acid was purified by fractional crystallization, sublimation under reduced pressure, and drying over sulfuric acid. Determinations of acidity and of bromine agreed with calculated values within 0.1 percent.

C.P. methanol was distilled over sodium and silver nitrate. Concentration of solution was checked by density measurements.

Glycine was purified by precipitation with alcohol from the aqueous solution, followed by three recrystallizations from water. A $1M$ solution had a conductivity of 9×10^{-6} mho and a pH of about 5.9.

Atlas commercial d-mannitol was recrystallized twice from water. Melting point 165.9°.

Dioxane and t-butanol were purified as described by Tomlinson,[5] t-butanol receiving two redistillations.

Ethylene glycol was stored for several days over calcium oxide and distilled under reduced pressure.

Clear potato starch solution (about 0.1 percent) was used as an indicator in iodine titrations. The sensitivity of the end point was roughly 10^{-7} mole per liter of iodine when $D>70$.

Thallous chloride was purified and prepared as described by Hogge and Garrett.[13]

Analytical reagent potassium iodate, used as a primary standard, was recrystallized, ground and dried at 150°. C.P. sucrose and neutral potassium iodide were used.

B. Methods

The experimental methods are those previously described by LaMer and Kamner[3] and Tomlinson[5] except as follows:

Reactions in high dielectric solvents were stopped by dilution and cooling with a mixture of starch solution and chopped ice, followed by immediate titration from a weight burette. Re-

actions in solvents of dielectric constant lower than 40 were stopped by addition of a measured amount of iodine solution from a carefully calibrated hypodermic syringe. The small excess of iodine was determined by measuring the transmittance of the solution at $\lambda = 3650$A with a Coleman spectrophotometer and comparing with a previously prepared curve, or by titration with dilute thiosulfate to 100 percent transmittance. The two methods gave identical results.

When either dioxane or glycine was the added solvent, a sodium thiosulfate solution in this mixture, containing any added lanthanum chloride, was mixed at zero time with a smaller quantity of a stronger sodium bromacetate solution in water only, without added solvent. This precaution was taken to avoid peroxide formation in dioxane and hydrolysis of bromacetate ion in the presence of glycine.

In glycine solutions it was important to add a little 0.1*N* acetic acid to the reaction mixture before titration.

The method of Hogge and Garrett[13] was employed in following thallous chloride solubilities.

The temperature of thermostats was determined to within 0.02° by means of a platinum resistance thermometer.

Values of the dielectric constant of glycine solutions have been specially re-determined for us by Dr. Jeffries Wyman, Jr.[23] Other values have been taken from the literature.[24]

C. Results

Data are presented in Table I for the bromacetate-thiosulfate reaction in water, glycine-water, methanol-water, and sucrose-water at 25° and 45° and for *t*-butanol-water, glycol-water, and mannitol-water at 25°; in the lower dielectric range constants have been obtained in *t*-butanol-water, dioxane-water mixtures at 25° and 45° and in dioxane-water with added lanthanum chloride (Table II). In glycine solutions at 45° a small drift with time was observed, which was apparently caused by a glycine catalyzed hydrolysis of bromacetate ion. A short extrapolation to zero time, the uncertainity of which is less than 1 percent, surmounted this difficulty. The drift can be accounted for by postulation of a side reaction, second order in bromacetate ion and glycine, with a specific rate constant of 5×10^{-4} liter per mole per minute.

TABLE I. Summary of data in high dielectric solvents.

Solvent	D	$\sqrt{\mu}$	k	$\log k_{\kappa=0}+1$	$1+\log k^{N}_{\kappa=0}$
		$T=25$°C $a=6.4$A			
16% Sucrose	74.7	0.1299	0.406	0.387	0.343
10% MeOH	74.1	.0815	.3220	.355	.327
20% MeOH	69.2	.0616	.2713	.302	.247
35% MeOH	61.9	.1446	.3337	.212	
35% MeOH	61.9	.1238	.308	.212	.098
35% MeOH	61.9	.0914	.269	.213	
8% *t*-Butanol	71.8	.0730	.3174	.356	.323
16% *t*-Butanol	64.9	.1460	.4127	.323	
16% *t*-Butanol	64.9	.1333	.3934	.320	.255
16% *t*-Butanol	64.9	.1090	.322	.322	
14.7% mannitol	76.4	.1390	.4265	.405	
14.7% mannitol	76.4	.1032	.381	.403	.363
14.7% mannitol	76.4	.0945	.371	.404	
26.4% glycol	70.9	.1660	.4630	.379	.305
2.309*M* glycine	131.5	.1666	1.021	.887	.857
2.309*M* glycine	inf.		extrapolated*		1.519
		$T=45$°C $a=6.8$A			
Water	71.66	0.1701	2.406	1.1226	
Water	71.66	.1722	2.413	1.1213	
Water	71.66	.2178	2.677	1.1183	
Water	71.66	.2639	2.954	*1.1223*	
Water	71.66	mean		1.1216	1.118
0.363*M* glycine	79.55	0.1991	3.101	1.234	1.225
1.00*M* glycine	93.37	.1412	3.54	1.394	
					1.379
1.00*M* glycine	93.37	.2447	4.25	1.395	
2.294*M* glycine	121.5	.1660	5.51	1.618	1.585
glycine	inf.				2.254
17.3% MeOH	63.8	.1988	2.276	1.019	0.962
31% sucrose	63.8	.1467	2.153	1.061	.960

* Compare Table III.

Recalculated data of LaMer and Kamner,[3] Straup and Cohn,[4] and Tomlinson[5, 6] are given in Table III. The data of Kappana[7] cannot be interpreted consistently and in particular his constants obtained in sucrose-water and ethanol-water mixtures cannot be extrapolated accurately to zero ionic strength, and are in disagreement with other work. They have, therefore, been omitted.

In Table IV are listed a few new determinations of the solubility of thallous chloride, together with some values from the literature.

DISCUSSION

A. The Bromacetate-Thiosulfate Reaction

In Figs. 1 and 2 $\log k_{\kappa=0}$ for the bromacetate-thiosulfate reaction is plotted against the reciprocal of the dielectric constant, with k calculated in 1 in the usual volume molar units, liters per mole per minute, and in 2 in the normalized mole fraction units of Eq. (3). The points obtained in glycine-water solutions lie on a straight line in both plots at 45° and 25°. When the solvents are

[23] Wyman, in press.
[24] Åkerlof, J. Am. Chem. Soc. **54**, 4125 (1932); Åkerlof and Short, *ibid.* **58**, 1241 (1936).

TABLE II. Summary of data obtained in low dielectric solvents.

$C_{LaCl_3}=0.642\times C_{Na_2S_2O_3}$ $t=25°C$			Dioxane-water mixtures	
D	Concentration $M/1\cdot10^4$	k_{-1} (min.$^{-1}$)	$\log \frac{M/l}{55.5}$	$\log k^N$
20.4	3.963	201.8	0.312	1.993
25.0	3.981	135.9	.275	1.858
29.7	3.984	90.8	.237	1.721
34.8	3.980	58.6	.203	1.565
		$t=45°C$		
20.2	3.920	873		
			0.299	2.643
20.2	3.907	878		
22.3	3.907	725	.280	2.580
30.1	3.895	363		
			.209	2.347
30.1	3.915	356		
		No $LaCl_3$ $t=25°C$		
20.1[a]	4.034	0.702	0.314	1.533
23.3[b]	20.95	.895	.373	1.579
25.3[b]	50.05	1.035	.349	1.666
		$t=45°C$		
20.0[a]	3.958	2.98	0.301	0.173
20.0[b]	20.55	4.93	.381	.312
21.8[b]	20.17	3.96	.357	.241
21.8[b]	49.58	5.67	.357	.397
23.2[b]	49.58	5.09	.339	.368

[a] Dioxane water. [b] t-Butanol water.

TABLE III. Summary of data recalculated and used for curves. $T=25°C$.

Observer	Solvent	D	$1+\log k_{\kappa=0}$	$1+\log k^N_{\kappa=0}$
K, F	water	78.54	0.399	0.398
K	1.47% sucrose	78.2	.401	.398
K	32.4% "	70.2	.368	.266
K	67.9% glycerol	56.5	.286	.012
K	3.73M urea	88.4	.555	.508
S	2.00M "	84.0	.478	.453
S	4.00M "	89.0	.557	.506
S	5.00M "	91.0	.584	.520
S	0.40M glycine	87.7	.522	.516
S	0.62M "	92.7	.577	.567
S	1.00M "	101.4	.669	.655
S	1.70M ethanol	74.0	.362	.333
S	3.41M "	69.2	.334	.276
S	5.11M "	64.3	.308	.220
T	2.60M glycine	138.1	.903	.869
T	2.80M "	142.6	.917	.880

K—Kamner, reference 3.
S—Straup, reference 4.
F—Fessenden [LaMer and Fessenden, J. Am. Chem. Soc. **54**, 2351 (1932)].
T—Tomlinson, reference 5.

aqueous mixtures of dielectric constant lower than that of water, a linear plot may or may not be obtained: if methanol-water solutions are used, the points obey the linear relation of Eq. (1) within the experimental error; if tertiary butanol is the added solvent, there is a slight upward curvature.

Comparison of Figs. 1 and 2 demonstrates that use of a mole fraction scale effectively eliminates most of the specific solvent differences evident in Fig. 1. The points obtained in water and in mixtures of water with glycine, sucrose, mannitol, or methanol are collinear after normalization; those obtained when the added solvent is ethanol, glycol, or glycerol show a slight deviation, while the points obtained in t-butanol-water mixtures lie appreciably above the others, but are much closer to the extrapolated high dielectric curve than when plotted on the volume-molar scale. The correction on the urea-points is too large, so that these lie below the common linear plot of Fig. 2. The values of the parameter, r_A+r_B, calculated from Figs. 1 and 2, (Table V) clearly illustrate the above conclusions.

While isodielectric methanol-water and sucrose-water solutions are, when k^N is used, equivalent solvents at 45° as at 25°, there remains a definite difference in the slopes of $\log k^N_{\kappa=0}$ *vs.* $1/D$ above and below the water point at the higher temperature. The value of r_A+r_B obtained from the high dielectric curve does not change significantly between 25° and 45°, while the value calculated from the sucrose-water points shows some temperature dependence. Such a temperature dependence suggests the existence of solvent effects not accounted for by Eq. (1) and not entirely removed by the use of k^N. The parameter r_A+r_B is a convenient catch-all for such effects.

A linear relation between $\log k^N_{\kappa=0}$ and $1/D$ does not disprove the existence of non-electrostatic effects. $1/D$ is very nearly linear in the mole fraction of such solvents as methanol,

TABLE IV. Solubility of thallous chloride.

Solvent	D	Solubility (moles/l)	Solubility $\times\frac{55.3}{\Sigma \text{ moles/l}}$
H_2O (reference 13)	78.54	0.01617	0.01617
H_2O	78.54	.01617	.01617
16% d-mannitol	76.1	.01688	.01869
8.3% glycol	76.1	.01530	.01613
2.7% t-butanol	76.1	.01466	.01494
5.5% methanol	76.1	.01373	.01419
4.2% ethanol (reference 13)	76.1	.01405	.01437
0.5M glycine	89.99	.01893	.01923
D_2O*	78.3	.01213	.01217

* Kingerley and LaMer, J. Am. Chem. Soc. **63**, 3256 (1941).

sucrose, glycol, ethanol, etc. (but not *t*-butanol) added to water, over a range from 0–40 percent or more. If there is a specific solvent effect, also linear in the mole fraction of added solvent, the plot of log $k^N_{\kappa=0}$ *vs.* $1/D$ may still be straight. The values of log $k_{D=\infty}$ and r_A+r_B obtained will, however, be in error and in general dependent on both solvent and temperature. The low and solvent-dependent values of r_A+r_B obtained from the kinetics of carbinol formation of dye ions[14,25] are apparently at least partly caused by such a linear solvent effect.

The data of Table I indicate that the Debye-Hückel extrapolation to zero ionic strength can be made satisfactorily when $D>60$. It seems likely, therefore, that the deviations from linearity in this range (Fig. 2) cannot be explained as the result of ion-association alone.

Tables VI and VII contain values of the energies and entropies of activation and of the "frequency factor" log B calculated from the Arrhenius equation and Eq. (8) using the data of Tables I, II and III and Figs. 2 and 3. A number of conclusions may be drawn:

In media of high dielectric constant the isodielectric B and $\Delta S^\ddagger$ are practically independent of D, T, or solvent used, whereas the constant composition B and $\Delta S^\ddagger$ decrease as D decreases. This decrease corresponds to a lowered probability of coordination of the like-charged reactant ions.

$\Delta E^\ddagger$ is temperature dependent when measured at constant composition, has a very slight dependence when measured in isodielectric media, and is practically independent of temperature when measured with the product DT held constant.

TABLE V. Values of slope log $k_{\kappa=0}$ *vs.* $1/D$.

T°C	Added solvent	Conc. scale	Slope	r_A+r_B (A)
25	glycine, sucrose, methanol, mannite	Normalized	−87.8	5.55
25	urea	Normalized	−69.1	7.04
45	glycine	Normalized	−81.4	5.62
45	sucrose, methanol	Normalized	−90.2	5.06
0	sucrose	Normalized	−75.8	6.43
25	mannitol	vol. molar	+18	−27
25	sucrose	vol. molar	−20.6	+23.6
25	*t*-butanol	vol. molar	−28.2	17.3
25	methanol	vol. molar	−54.9	8.9
25	glycine	vol. molar	−94.0	5.18
45	sucrose	vol. molar	−35.3	12.9
45	methanol	vol. molar	−59.5	7.7
45	glycine	vol. molar	−91.3	5.34
0	sucrose	vol. molar	−13.8	39

[25] Hochberg and LaMer, J. Am. Chem. Soc. **63**, 3110 (1941).

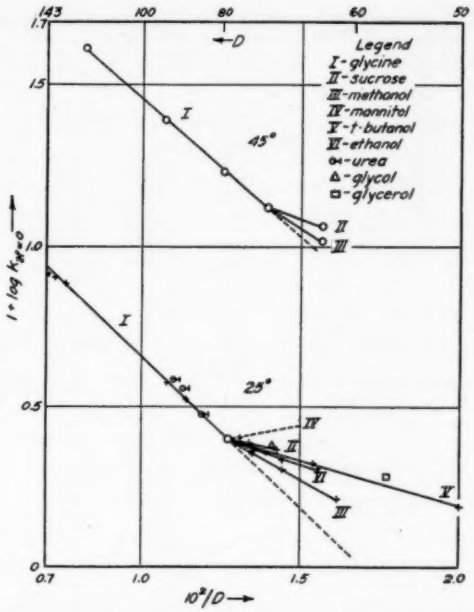


FIG. 1. Volume molar rate constant $k_{\kappa=0}$ (in min.$^{-1}$) for bromacetate-thiosulfate reaction as function of temperature and dielectric constant.

$\Delta S^\ddagger$, calculated from the data for the lanthanum ion catalyzed reaction at a low constant ionic strength with dielectric constant of 20 to 35, decreases in absolute value (becomes less negative) as D decreases. This corresponds to a negative ionic strength effect consistent with

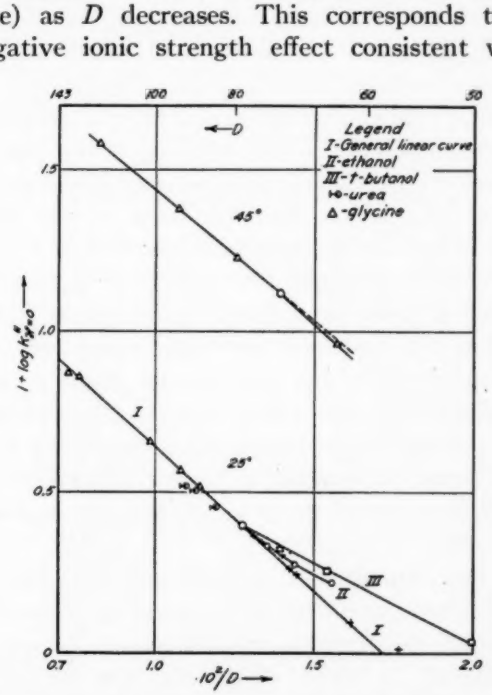


FIG. 2. Normalized mole fraction rate constant $k^N_{\kappa=0}$ (in min.$^{-1}$) for bromacetate-thiosulfate reaction as function of temperature and dielectric constant.

TABLE VI. Energies and entropies of activation in media of high dielectric constant. k^N(min.$^{-1}$) $\kappa=0$.

Range	Solvent added to water	D(25°)	$\Delta E^{\ddagger}$	$\log_{10} B$	$-\Delta S^{\ddagger}$ cal./deg.
		Constant Composition			
0–25°	none	78.54	15,730	10.94	18.5
0–25°	32.4% sucrose	70.2	15,530	10.64	19.9
25–45°	none	78.54	15,640	10.94	18.7
25–45°	32.4% sucrose	70.2	14,850	10.19	22.1
25–45°	17.3% methanol	70.5	14,980	10.26	21.8
25–45°	1*M* glycine	101.4	15,660	11.12	17.8
25–45°	2.3*M* glycine	131.3	15,850	11.47	16.2
		Constant Dielectric			
0–25°	glycine	88.06	17 530	12.35	12.1
0–25°	sucrose	78.54	17,530	12.26	12.5
25–45°	glycine	78.54	17,720	12.38	12.1
25–45°	glycine	88.06	17,530	12.36	12.2
25–45°	sucrose-methanol	71.66	17,920	12.41	11.9
25–45°	*t*-butanol	71.66	17,270	11.97	14.0
25–45°	glycine	inf.	15,960	12.23	12.8
		Constant (*DT*)			
0–25°	glycine	80.67	16,180	11.30	16.9
0–25°	sucrose	71.9	16,030	11.05	18.0
25–45°	glycine	78.54	16,200	11.27	17.2
25–45°	sucrose	70.2	16,170	11.14	17.7
25–45°	glycine	inf.	15,960	12.23	12.8

previous conclusions[5,6] that the reaction is between the positive complex ion $La^{+++}\cdot S_2O_3^{=}$ and the negative $BrAc^{-}$. $\Delta E^{\ddagger}_{\text{const } D}$ is independent of dielectric constant, while $\Delta E^{\ddagger}_{\text{const } DT}$ decreases slightly as D decreases. This might be caused by a positive non-electrostatic effect and a corresponding dependence of parameters on temperature.

When no lanthanum chloride is added a value of $\Delta E^{\ddagger}_{\text{const } DT}$ is obtained (Table VII) almost identical with that obtained for the catalyzed reaction. From this we conclude that the great increase in the reaction rate when lanthanum ion is present is purely an electrostatic effect. The value of $\log B_{\text{const } DT}$, on the other hand, is over two units higher for the catalyzed reaction.

$\Delta E^{\ddagger}_{\text{const } DT}$ is about 1000 cal. lower in the low dielectric media than in the high dielectric media studied. This indicates that there may be an important positive non-electrostatic effect in the dioxane-water and *t*-butanol-water mixtures and that the upward curvature of the plot of $\log k$ *vs.* $1/D$, found by Tomlinson[5,6] is not due entirely to the uncertainty of the extrapolation to zero ionic strength.

If the value of nN_w/N_0 in Eq. (12) is taken as 1/55.5, and the entropy factor is taken as one, the value of the isodielectric frequency factor B calculated is only about 0.0–0.6 log unit larger than that experimently obtained, whereas Eyring's estimates from the transition state theory[26] for two reacting polyatomic molecules call for an entropy factor of 10^{-5}–10^{-10}. This apparent disagreement is typical of reactions involving ions and is presumably the result of large entropies of vaporization and large solvent and solvation effects. The agreement with predictions of the collision theory is probably quite fortuitous; for many non-ionic reactions and for some ionic reactions (see, for example, reference 25) it is very poor.

B. Effect of Choice of Concentration Scale upon Interpretation of Other Reaction Rates

Search of the literature reveals some previous data, the interpretation of which might be affected by a change to the mole fraction concentration scale. Two interesting cases are discussed in Sections (C) and (D). Straup and Cohn[4] have studied the bromacetate-thiosulfate reaction in mixtures of water, ethanol, and either glycine or urea, iso-dielectric with water, with results consistent with those already discussed; the mole fraction constant is about the same in the iso-dielectric solvents, but appreciably low in the urea mixtures.

For a reaction between *an ion* and *a neutral molecule*, the importance of the dielectric constant will depend upon the geometry of the critical complex. If the reactants can be considered as two particles approaching each other and forming

TABLE VII. Energies and entropies of activation in media of low dielectric constant. k^N in min.$^{-1}$, $t=25°-45°$.

Solvent added to water	Concentration of reactants	D	$\Delta E^{\ddagger}$	$\log B$ (min.)$^{-1}$	$-\Delta S^{\ddagger}$ cal./deg.
		Constant Composition			
49.43% dioxane; $LaCl_3$	3.9	34.8	16,980	14.03	4.5
61.09% dioxane; $LaCl_3$	3.9	25.0	15,720	13.38	7.8
63.80% dioxane; $LaCl_3$	3.9	22.7	15,640	13.37	7.9
66.50% *t*-butanol; No $LaCl_3$	20.5	23.3	15,960	11.29	17.1
63.80% *t*-butanol; No $LaCl_3$	50.5	25.3	15,890	11.34	16.8
		Constant Dielectric			
dioxane; $LaCl_3$	3.9	20.2	13,960	12.21	12.8
dioxane; $LaCl_3$	3.9	22.3	14,000	12.19	12.9
dioxane; $LaCl_3$	3.9	25.0	13,940	12.04	13.6
dioxane; $LaCl_3$	3.9	30.1	13,940	11.92	14.2
dioxane; No $LaCl_3$	3.9	20.0	13,810	9.66	24.5
t-butanol; No $LaCl_3$	20.5	23.3	13,370	9.36	25.9
		Constant (*DT*)			
dioxane; $LaCl_3$	3.9	32.1	15,230	12.78	10.3
dioxane; $LaCl_3$	3.9	26.7	14,970	12.77	10.3
dioxane; $LaCl_3$	3.9	23.8	14,990	12.86	9.9
dioxane; $LaCl_3$	3.9	21.6	14,900	12.86	9.9
t-butanol; No $LaCl_3$	20,5	23.3	14,480	10.18	22.2
t-butanol; No $LaCl_3$	50.5	25.3	15,070	10.70	19.8

[26] Glasstone, Laidler, and Eyring, reference 17, p. 19.

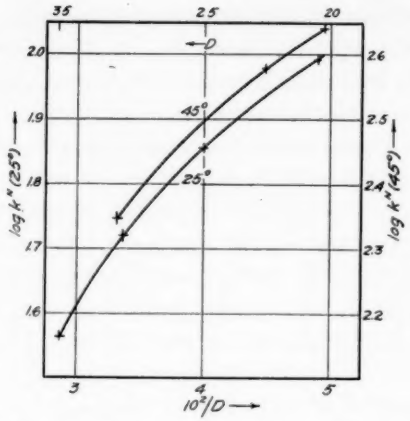


FIG. 3. Effect of dielectric on La^{+++} catalyzed reaction.

a double-sphere critical complex such as that of Eq. (1), with the charge continuing to be centered on the reacting ion, little effect will be expected. This is an extreme case. The opposite extreme, in which the critical complex can be represented as a single sphere with the charge symmetrically distributed about its center leads to the equation[27]

$$\ln k_{\kappa=0} = \ln k_{D=\infty} + \frac{Z_A^2\epsilon^2 N_{Av}}{2DRTr_A} - \frac{Z_A^2\epsilon^2 N_{Av}}{2DRTr_X}. \quad (13)$$

Since r_x is greater than r_A Laidler and Eyring conclude that the rate of a reaction between an ion and a neutral molecule should increase with decreasing dielectric constant.

As the actual case probably lies somewhere between these extremes, Eq. (13) should predict a self-potential effect of the right sign but too large. The experimental examples suggested[27,28] are not entirely convincing. The supposed dielectric constant effect on the reactions between water and a sulfonium cation[29] and between alkyl halides and halide ions[30] is so large that one suspects other effects may be very important. On the other hand, the reaction between hydroxyl ion and isopropyl bromide, studied[31] in 60 percent and 80 percent ethanol solutions is significantly faster in the latter solvent only when volume molar concentration units are used. On a mole fraction basis the "effect" will evidently become of the wrong sign at a temperature slightly below those used for the measurements (Table VIII). Probably no definite conclusions as to the importance of dielectric constant effects should be drawn until it is possible to separate the non-electrostatic effects.

There are, however, at least two similar cases in which this can be accomplished in part. The increase of the rate of reaction between thiosulfate ion and methyl bromacetate[5,6] when *t*-butanol is added to the water-solvent, is more than removed by conversion to a mole fraction scale. Comparison with the observed solvent effects on the corresponding reaction with bromacetate ion suggests that in this case the self-potential effect is unimportant. The reaction between alkyl halides and thiosulfate ion has been studied[4] in water, in mixtures of water with ethanol, glycine, and urea, and in mixtures of water, ethanol, and either glycine or urea isodielectric with water (Table IX). The results indicate a small self-potential effect of the sign predicted by Eq. (12) when glycine or urea is added, although this is only evident in the latter case when the mole fraction scale is used. When ethanol is the added solvent a similar effect appears to be present, but is far less important than another solvent effect.

C. The Quenching of Fluorescence

The quantity $(I_0/I-1)/C_Q=k_Q$ is obtained[32] from studies of the quenching of fluorescence in solution. I_0 is the intensity of fluorescent light emitted by a solution before addition of a

TABLE VIII. Effect of solvent upon reaction between isopropyl bromide and hydroxyl ion, from data of Hughes, Ingold, and Shapiro, reference 31.

t°C	Medium	D	k	k^N (60% ethanol)
80	80% Ethanol	23.20	4.61	3.52
80	60% "	31.82	3.11	3.11
50	80% "	28.10	0.241	0.184
50	60% "	37.72	.181	.181
35	80% "	30.8	.0477*	.0345*
35	60% "	41.1	.0368*	.0368*

* Values obtained by extrapolation.

[27] Laidler and Eyring, Ann. N. Y. Acad. Sci. **39**, 303 (1940).
[28] Glasstone, Laidler, and Eyring, reference 17, p. 439 seq.
[29] Hughes and Ingold, J. Chem. Soc. (London), 1571 (1933).
[30] Bergmann, Polanyi, and Szabo, Zeits. f. physik. Chemie B20, 161 (1933).
[31] Hughes, Ingold, and Shapiro, J. Chem. Soc. (London), 225 (1936).
[32] Wawilow and Frank, Zeits. f. Physik **69**, 100 (1931).

TABLE IX. Effect of solvent upon reaction between methyl iodide and thiosulfate ion, from data of Straup and Cohn, reference 4. $CH_3I+S_2O_3^{=}\rightarrow CH_3S_2O_3^{-}+I^{-}$. $t=25°C$.

Medium	D	$\log k-\log k_{H_2O}$	$\log k^N-\log k_{H_2O}$
20% ethanol	69.5	0.241	0.183
0.4M glycine in 20% ethanol	78.5	.204	.141
0.4M glycine	87.7	− .054	− .060
30% ethanol	64.5	+ .395	+ .307
0.62M glycine in 30% ethanol	78.5	+ .241	+ .145
0.62M glycine	92.7	− .74	− .75
5M urea in 30% ethanol	78.5	+ .353	+ .21
5M urea	91.0	+ .022	− .042

quenching material and I is the intensity at a concentration C_Q of quencher. A constant source of illumination is used, and the molar concentration of fluorescent material is in general much smaller than that of quencher. To show that k_Q is proportional to the second-order rate constant for the quenching reaction, we need make no assumptions concerning the mechanism[32–35] beyond that the process of activation of a molecule F by a light source, the emission of fluorescent light, and the deactivation of an activated molecule by a quenching molecule may be represented by equations of the following type:

$F+h\nu\xrightarrow{k_1}F^{\ddagger}$ zero order for constant C_F and constant light source,

$F^{\ddagger}\xrightarrow{k_2}F+h\nu$ first order in $F^{\ddagger}$,

$F^{\ddagger}+Q\xrightarrow{k_3}F+Q+$Energy second order in $F^{\ddagger}$ and Q.

Since I is independent of time a steady state exists.

$$dC_{F^{\ddagger}}/dt=0=k_1-k_2C_{F^{\ddagger}}-k_3C_{F^{\ddagger}}C_Q. \quad (14)$$

We choose the units of k_1 and k_2 so that I and I_0, in Einsteins per second, are given by

$$I_0=k_1, \quad (15)$$

$$I=k_2C_{F^{\ddagger}}. \quad (16)$$

Substituting $C_{F^{\ddagger}}$ from Eq. (14), we have

$$\left(\frac{I_0}{I}-1\right)\Big/C_Q=\left(\frac{k_1}{k_2C_{F^{\ddagger}}}-1\right)\Big/C_Q=\frac{k_3}{k_2}=k_Q. \quad (17)$$

To obtain k_3 the true rate constant of the quenching reaction from k_Q, it is necessary to multiply by k_2. This is equivalent to dividing by the mean life of fluorescence, a quantity which may be determined for any particular fluorescent substance by direct optical measurement,[36] or indirectly by studying the effect of viscosity on the polarization of the fluorescent emission.[37,38] Since quenching has an activation energy of about 4 kcal., i.e., similar to that of diffusion, a linear relation between k_Q and diffusion (fluidity) has been postulated by many authors,[32,38,39] but experimental curves show deviations from linearity (see Fig. 4.1) which have not received satisfactory explanation.

When the reactants are ions, the almost obvious dependence upon ionic strength has been observed.[40,41] There is also a self-potential effect. In this connection it should be pointed out that any attempt[40] to base a decision of the mechanism between the concept of "an ordinary bimolecular reaction between the quenching ion and the activated dye molecule" and that of "de-activation of the photo-activated molecule by collision with the quenching ion in which some energy is transferred to the quencher" by testing the agreement with the Brönsted activity coefficient factor is doomed to failure. The number of effective collisions is *not* determined by the activities of the colliding molecules *alone*. Brönsted's equation can be justified equally well from an equilibrium viewpoint as from a purely collisional or diffusional viewpoint. (Reference 3, p. 2668.)

Since most investigators of fluorescence quenching have been unaware of the importance of these electrostatic complications, there are few data in the literature that can be interpreted unambiguously. It is evident, however, that the plot of k_Q *vs.* fluidity $(1/\eta)$ is never linear, whether the viscosity (η) is varied by changing the medium, or by varying the temperature. Figures 4 to 7 demonstrate that when the medium is varied at constant T, use of the normalized mole fraction

[33] Weiss, Trans. Faraday Soc. **35**, 48 (1939).
[34] Bowen, Trans. Faraday Soc. **35**, 15 (1939).
[35] Rollefson and Stoughton, J. Am. Chem. Soc. **63**, 1517 (1941).
[36] Gaviola, Zeits. f. Physik **42**, 853, 862 (1927); Szymanowski, *ibid.* **95**, 440 (1935).
[37] F. Perrin, Thesis, Paris, France (1929).
[38] Wawilow, Acta. Physicochim. U.S.S.R. **7**, 49 (1937).
[39] Svešnikov, Acta Physicochim. U.S.S.R. **7**, 755 (1937).
[40] Stoughton and Rollefson, J. Am. Chem. Soc. **61**, 2634 (1939).
[41] Stoughton and Rollefson, J. Am. Chem. Soc. **62**, 2264 (1940).

constant k_Q^N reduces the curvature considerably.*

The quenching of fluorescein[39] (Fig. 7) and of rhodamine-B[32] (Fig. 6) by potassium iodide are ionic reactions. The most interesting result in the latter case is that obtained when pure methanol is the solvent. In this case k_Q is found to be much greater than in water, although iodide ion is known to diffuse more slowly in methanol. After normalization the ratio of k_Q in water and in methanol is 1.40, while the ratio of the mobilities of iodide ion is 1.25 and of the diffusion constants of potassium iodide is 1.26.

The quenching of acridone by potassium iodide[41] and the quenching of rhodulin red by aniline[39] involve a neutral molecule and should be much less dependent upon dielectric constant. In both cases the plot of k_Q^N *vs.* $1/\eta$ is linear. The case of rhodulin red is particularly interesting, since the quencher is the comparatively large and neutral aniline molecule, which might be expected to obey Stokes' law, and since pure alcohols were used as solvents.

It can hardly be a coincidence that the percent deviation from a straight line through the origin of points, obtained in a series of alcohols of molecular weights ranging from 32 to 85, should be closely proportional to the molecular weights. It is to be noted that the anomaly in the order of the points obtained in isobutyl and isoamyl alcohols is removed by normalization to the mole fraction scale.

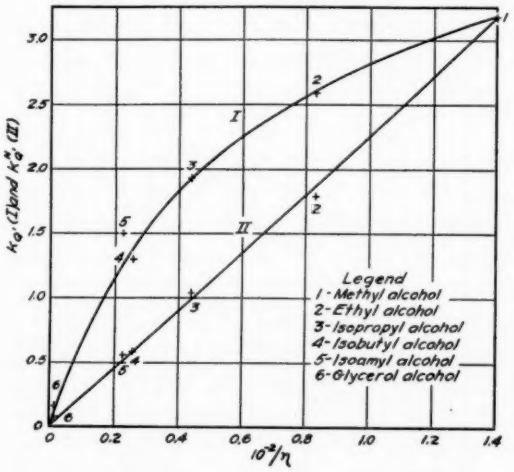


FIG. 4. The quenching of fluorescence of rhodulin red by aniline. Data of Svešnikov.

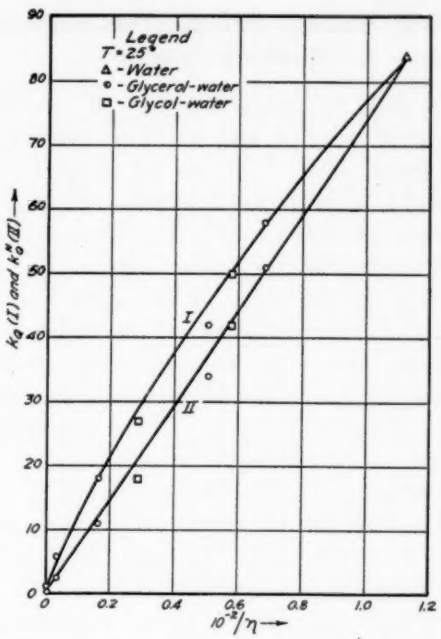


FIG. 5. The quenching of fluorescence of acridone by potassium iodide. Data of Stoughton and Rollefson.

The significance of this linear plot is not entirely clear, and cannot be explained, at least until a thorough experimental analysis of the problem, involving a determination of diffusion coefficients, has been made. It must be emphasized that a mere change of scale cannot reduce the curvature of the plot of k *vs.* $1/\eta$ when the latter is varied by changing the temperature and holding the solvent composition constant; and in the case of the quenching of rhodulin red by aniline, certain points obtained in glycerol-ethanol mixtures fall on a smooth curve with the points obtained in pure solvents before normalization to a mole fraction scale, but apparently do not fall on the linear plot after normalization.

Nevertheless the quenching of fluorescence is an example of a type of reaction in the study of which the concentration scale is very important and for which we find use of the mole fraction scale gives a simple result. Quenching involves a diffusion process as a rate determining step. Experiments are in progress to determine, if possible, whether the cage model Eq. (10) or the Smoluchowski type equations fit the data best.

* The symbol $k_{Q'}$ or $k_{Q'}{}^N$, used in the figures, denotes the first-order constant $(I_0/I-1)$ obtained with C_Q held constant.

D. Other Solvent Effects. The Solubility of Thallous Chloride

The rate of isomerization of ammonium cyanate[15,42] and of the carbinol formation of bromphenol blue[14,15] is slower in glycol-water mixtures than in the isodielectric methanol-water solutions. In such a case it is evident that use of k^N will make the discrepancy worse. The order, by effect on the rate, of the added solvents, methanol, ethanol, glycol, is the order of their increasing molecular weights and viscosities;[15] but whether we reason from an equilibrium rate theory or from Eq. (9) we must conclude that viscosity cannot directly affect the rate, since large energies of activation are involved.

If the equilibrium theory of reaction rate is correct, solvent effects should not be peculiar to ionic kinetics, but should be found for ionic equilibria in general. We have, therefore, measured the solubility of thallous chloride in several isodielectric solvents (Table IV). While no such extended analysis as that given by Hogge and Garrett[13] for ethanol-water mixtures has been attempted, it is possible to draw certain conclusions:

The solubility cannot be predicted unambiguously from the dielectric constant. It depends upon the solvent added to water and increases in the order of added solvents methanol, ethanol, *t*-butanol, glycol, mannitol. This is consistent with a *decrease* in reaction rates, which involve the factor $f_A f_B / f_X$. A general decrease in the activity coefficients, corresponding to a proportional increase in the solubility of reactants *and critical complex*, would decrease the reaction rate. The solubility of thallous chloride in water is actually increased by adding mannitol. Dielectric constant effects are here of less importance than another effect, apparently related to the size of the mannitol molecule. The addition of glycine increases the solubility, but less than would be predicted from the ethanol-water data.

CONCLUSIONS

One conclusion may be drawn; namely, that use of the mole fraction scale instead of the volume molar scale leads to distinctly simpler and more consistent results in various solvents in the specific case of the bromacetate-thiosulfate reaction.

The more general conclusion, that the mole fraction scale should always be used in comparing rate constants in different solvents, is in a sense an academic one requiring no experimental verification. As Scatchard clearly states[1] the only object is to choose that scale which will allow the specific solvent effects to be most readily accounted for by activity coefficients determined by the physical properties of solute and solvent.

The basis of any mole fraction ideal law of solution is the assumption that the number of available positions in a liquid is proportional to the total number of molecules present and that all positions are equally available for all molecules, regardless of size or shape. Then any size-shape effects must be compensated for by activity coefficients. If there are other deviations from ideality, i.e., if the forces between solvent-solvent, solvent-solute, and solute-solute pairs of molecules are appreciably different, these deviations must also be compensated by an activity coefficient.

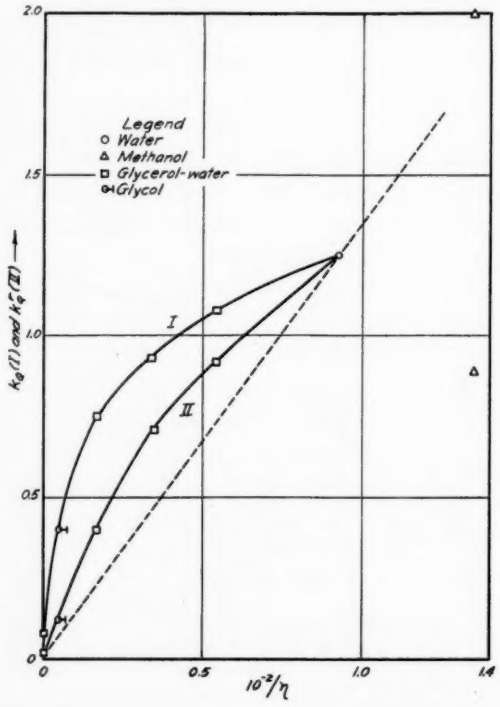


FIG. 6. The quenching of fluorescence of rhodamine B by potassium iodide. Data from Frank and Wawilow.

[42] Svirbely and Schramm, J. Am. Chem. Soc. **60**, 330 (1938); Lander and Svirbely, *ibid.* **60**, 1613 (1938).

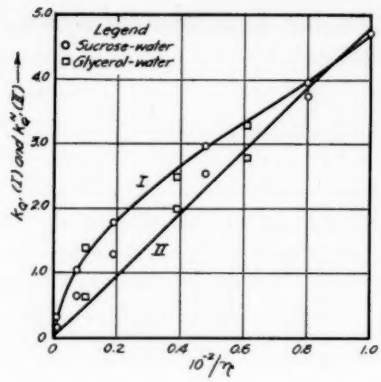


FIG. 7. The quenching of fluorescence of fluorescein by potassium iodide. Data from Svešnikov.

There are no equations available for precise calculation of non-electrostatic activity coefficients. The approximate equation valid, for "regular" solutions[27]

$$RT \ln \gamma_1 = v_1 \left(\frac{N_2 v_2}{N_1 v_1 + N_2 v_2} \right)^2 \times \left[\left(\frac{E_{11}}{v_1} \right)^{\frac{1}{2}} - \left(\frac{E_{22}}{v_2} \right)^{\frac{1}{2}} \right]^2, \quad (18)$$

where the subscripts 1 and 2 refer to solute and solvent, respectively, N = mole fraction, v = molar volume, and E's are potential energy terms that may be replaced by the energies of vaporization of the pure liquids, predicts a relationship between solvent effects and the ratio E_{22}/v_2. This however does not vary significantly in the aqueous mixtures discussed in this paper.

Except in certain special cases the effect of differences in size of solvent and solute molecules cannot be neglected. In the case of approximately rod-shaped molecules it has been shown theoretically and experimentally[43,44] to be zero: Thus, *n*-hexane and *n*-hexadecane obey the mole fraction ideal laws throughout the entire range of concentration. For other shapes, it has been suggested[45,46] that there may be large deviations from the mole fraction laws and that these deviations are an increasing function of the ratio of the molar volumes of solute and solvent. For spherical molecules A and B with $v_A = 1/2 v_B$, the equations of Chang lead to a value of about 0.8 for the activity coefficient of the very dilute solute, A.[47]

The simplicity of the results found for the bromacetate-thiosulfate reaction must be due to a considerable cancellation of the non-electrostatic activity coefficients of the reactants with those of the critical complex. No such cancellation is likely in the case of solubility or for a reaction such as the carbinol formation of brom-phenol blue[14] in which the critical complex closely resembles one of the reactants.

[43] Hildebrand, J. Phys. Chem. **43**, 109 (1939); Hildebrand and Sweney, *ibid.* **43**, 297 (1939).
[44] Hildebrand, J. Am. Chem. Soc. **59**, 794 (1937).
[45] Fowler and Rushbrooke, Trans. Faraday Soc. **33**, 1272 (1937).
[46] Chang, Proc. Camb. Phil. Soc. **35**, 265 (1939).
[47] Fowler and Guggenheim, *Statistical Thermodynamics*, (Cambridge University Press, 1939) p. 366.

SUMMARY

New data are presented to emphasize the difficulties of comparing reaction rate constants obtained in different solvents. It is shown that use of a mole fraction concentration scale instead of the usual volume molar scale gives a simpler result for the kinetics of the bromacetate-thiosulfate reaction.

Temperature coefficients have been determined for this reaction and are discussed as criteria of electrostatic and non-electrostatic effects.

It is suggested that determination of the energy and entropy of activation with the product DT and the concentration of reactants held constant helps in interpreting the kinetics of ionic reactions.

Data on the solubility of thallous chloride in solvents of different molecular volume are presented to show that there are other specific solvent effects as important as the electrostatic effects.

Examples of the effect of choice of concentration scale upon the interpretation of data are taken from the literature. The quenching of fluorescence in solution as determined by the viscosity is discussed.

The Derivation of a General Kinetic Equation for Reaction Between Ions and Dipolar Molecules

EDWARD S. AMIS AND GEORGE JAFFÉ
Louisiana State University, Baton Rouge, Louisiana

(Received April 1, 1942)

An equation has been derived for the reaction rate constant in the case of ion-dipole reactions. Section II contains the extension of Debye-Hückel's theory of ionic atmospheres to the case of dipoles surrounded by ions, coupling it with Onsager's theory of electric moments of molecules in liquids. Section III applies the potential constructed to the derivation of the rate constant by the kinetic procedure of Christiansen and Scatchard. The result is substantiated by existing data both from concentration and dielectric constant dependence of the rate of reaction between ions and dipoles (Section IV).

I. INTRODUCTION

SINCE the formulation of the law of mass action and the promulgation of the theory of temperature coefficients, the two outstanding contributions to the theory of the kinetics of reactions in solution have been the application by Brönsted[1] of the theory of Debye and Hückel to reaction rates, and Scatchard's[2] development of the effect upon reaction velocities of changing solvent insofar as this effect is due to changing dielectric constant. These two contributions were applicable to the case of reactions between ions and led to the general kinetic equation

$$\ln k = \ln k_\infty - \frac{z_A z_B \epsilon^2}{DkTr_0} + \frac{z_A z_B \epsilon^2}{DkT} \frac{\kappa}{1+a\kappa}, \qquad (1)$$

which has become so familiar to those who read kinetic literature.

The authors, studying the reactions between charged ions and dipolar molecules, have become convinced that a similar equation expressing the concentration and dielectric effects upon ion-dipole reactions in solution should be available to kineticists. This paper has as its object, therefore, the derivation of such an equation together with its experimental verification insofar as existing data permit.

II. THE IONIC ATMOSPHERE AROUND A DIPOLAR MOLECULE

In determining the ionic atmosphere around a dipolar molecule we shall disregard the interaction between dipoles. Under this restriction the differential equation for the potential ψ_0 in the neighborhood of any one dipolar molecule will be the same as for the potential around an ion. It is only with regard to the boundary conditions at the surface of the molecule that the two problems differ.

We shall assume that there are s different species of ions. Let z_i be the valency of the species i and let n_i be their number per cm^3. Then the differential equation for ψ_0 becomes, with the usual restriction to small values of ψ_0,

$$\nabla^2\psi_0 = \kappa^2\psi_0, \qquad (2)$$

where κ is the well-known parameter of the theory of Debye-Hückel[3] and is of the dimension of a reciprocal length:

$$\kappa^2 = (4\pi\epsilon^2/DkT)\sum_{i=1}^{s} n_i z_i^2. \qquad (3)$$

Here ϵ signifies the elementary charge and D the dielectric constant of the solvent.

As the Eq. (2) can be "separated" in spherical coordinates it is easy to obtain a general solution which can be adapted to any distribution of point charges within the molecule. However, we shall be satisfied to treat the dipole as a point singularity. Then a suitable particular solution of (2) can be obtained in a very direct way by "polarizing" the solution of Debye and Hückel. This is, for the case of an ion,

$$\psi_0 = A_0 e^{-\kappa r}/r. \qquad (4)$$

[1] J. N. Brönsted, Zeits. f. physik. Chemie **102**, 169 (1922); **115**, 337 (1925).
[2] G. Scatchard, Chem. Rev. **10**, 229 (1932).
[3] P. Debye and E. Hückel, Physik. Zeits. **24**, 185 (1923). See also Hans Falkenhagen, *Elektrolytes*, English translation by R. P. Bell (Clarendon Press, Oxford, 1934), Chapter VII.

Let the position of the dipole coincide with the origin and its direction with the positive z axis. Let, furthermore, the shape of the dipole-molecule be idealized by a sphere of radius a. Then we obtain an adequate solution for $r \geq a$, i.e., a solution that has the same angular dependence as a dipole-potential, by differentiating (4) partially with regard to z. Doing this and substituting in the result for z the expression $r \cos \vartheta$ (the angle ϑ being counted from the positive z axis) we obtain

$$\psi_0 = A(e^{-\kappa r}/r^2)(1+\kappa r) \cos \vartheta, \quad r \geq a. \tag{5}$$

As for the interior of the dipole molecule we might follow the procedure of Debye and Hückel by determining ψ_i there from the differential equation

$$\nabla^2 \psi_i = 0, \quad r \leq a \tag{6}$$

and retaining the constant value D also for the interior. The condition to be imposed on ψ in this domain is that it should be continuous except for a singularity at the origin corresponding to a dipole of the given strength.

If this is done a reasonable formula for the ionic atmosphere is obtained. However, a comparison with experimental kinetic data (see Section IV) shows that, in order to obtain agreement, the dipoles have to be chosen of the order 10×10^{-18}, i.e., five to ten times too large. The reason for this discrepancy is evidently that in the indicated procedure the interaction between the dipole and the dielectric solvent is not properly accounted for.

From Onsager's theory of electric moments of molecules in liquids[4] it follows that any one immersed dipole acts upon distant charges with an "external moment" different from its moment in vacuum. The intervening medium has the effect of "enhancing both the permanent and the induced dipole moments." We are, therefore, going to combine Debye-Hückel's theory of ionic atmospheres with Onsager's model of a dipole immersed in a dielectric liquid.

In accordance with Onsager we retain the spherical shape of the molecule and characterize it by its permanent moment μ_0 (in vacuum) and its polarizability α. This is to be related to an "internal refractive index n" by

$$\alpha = ((n^2-1)/(n^2+2))a^3. \tag{7}$$

The problem to be solved is the following: a solution of (6) having a dipole singularity at $r=0$ has to be joined to our solution (5) in the proper way (see reference 4, p. 1488) at $r=a$. This involves a determination of the external characteristic moment μ^* such as it becomes under the action of the polarization created by itself.

First we solve the problem which presents itself if a rigid dipole of moment m is introduced into a cavity of radius a. For the exterior the solution given by (5) is to hold; for the interior the solution

$$\psi_i = (m/r^2 + Br) \cos \vartheta, \quad r \leq a \tag{8}$$

meets the requirements. From the usual boundary conditions for the electrostatic field the constants A and B are determined as

$$A = 3me^{\kappa a}/(D(2+2\kappa a+\kappa^2 a^2)+(1+\kappa a)) \tag{9a}$$

and

$$B = -(m/a^3)(D(2+2\kappa a+\kappa^2 a^2)-2(1+\kappa a))/(D(2+2\kappa a+\kappa^2 a^2)+(1+\kappa a)). \tag{9b}$$

Now m remains to be determined as a function of μ_0 and n^2. This determination has to be based on the "condition for internal equilibrium" (Onsager, reference 4, p. 1488):

$$m = \mu_0 + \alpha F_z, \tag{10}$$

where the force F_z is the force acting on the dipole owing to the polarization created by itself. This force is found to be

$$F_z = -\frac{\partial}{\partial z}(\psi_i - m \cos \vartheta/r^2) = -B. \tag{11}$$

Making use of (7) and (9b) we obtain

$$m = \mu_0(n^2+2)(D(2+2\kappa a+\kappa^2 a^2)+(1+\kappa a))/3(D(2+2\kappa a+\kappa^2 a^2)+n^2(1+\kappa a)). \tag{12}$$

With this value introduced into (9a) the potential of the ionic atmosphere around a dipolar molecule of moment μ_0 can finally be written in the form

$$\psi_0 = (\mu^* e^{-\kappa r}/Dr^2)(1+\kappa r) \cos \vartheta, \tag{13}$$

[4] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

where μ^*, the "external moment," is given by

$$\mu^*=\mu_0(n^2+2)De^{\kappa a}/(D(2+2\kappa a+\kappa^2a^2)+n^2(1+\kappa a)). \quad (14)$$

In the absence of an ionic atmosphere, i.e., for $\kappa\rightarrow 0$, this solution and the corresponding one for ψ_i reduce to Onsager's solution, as they should. For $n^2\rightarrow 1$ Eqs. (13) and (14) represent the simpler case where the molecule has a permanent dipole but no polarizability.

III. THE KINETIC EQUATION

We shall now apply the potential constructed in Section II to calculate the rate of formation of an intermediate complex X formed out of a dipole molecule A of moment μ_0 and an ion B of charge ϵz_B. In doing so we are going to follow the procedure of Christiansen and Scatchard.[5] However, it must be taken into account that the potential does not depend on r only but also on ϑ.

Let C_x, C_A, and C_B be the concentrations of X, A, and B, respectively, and let us introduce polar coordinates r, ϑ, φ about the center of a dipole A. The probability of finding an ion B in a specified element of volume characterized by the limits r and $r+dr$, ϑ and $\vartheta+d\vartheta$, φ and $\varphi+d\varphi$, will then, by Boltzmann's theorem, be proportional to

$$C_AC_B\exp(-\psi_0\epsilon z_B/kT)r^2\sin\vartheta dr d\vartheta d\varphi. \quad (15)$$

In order to obtain the rate of formation of X, and thereby the velocity of reaction, some criterion for the formation of X must be established. This can be done in two different ways. Either it is assumed that there are "sensitive zones" on the exterior of the molecule. Whenever one of these areas is touched by an ion B the formation of X ensues. Or it is assumed that there is a critical distance for each direction.

Let us follow the first alternative. This amounts to assuming that r, ϑ, φ have to assume specified values between comparatively narrow limits: r_0 and $r_0+\Delta r_0$, ϑ_0 and $\vartheta_0+\Delta\vartheta_0$, φ_0 and $\varphi_0+\Delta\varphi_0$. We shall assume rotational symmetry of the molecule about the z axis. Then φ need not be specified and (15) can be integrated with regard to φ. Consequently the expression for the concentration of the complex becomes

$$C_x=2\pi k'C_AC_Br_0^2\sin\vartheta_0\Delta r_0\Delta\vartheta_0\times\exp(-\epsilon z_B\psi_0/kT), \quad (16)$$

where k' is a constant.[6]

Setting

$$K=2\pi k'r_0^2\sin\vartheta_0\Delta r_0\Delta\vartheta_0 \quad (17)$$

we obtain

$$\ln(C_x/C_AC_B)=\ln K-\epsilon z_B\psi_0(r_0,\vartheta_0)/kT. \quad (18)$$

In the limiting case $\kappa\rightarrow 0$ this reduces to

$$\ln(C_x^0/C_A^0C_B^0)=\ln K-\epsilon z_B\mu_0^*\cos\vartheta_0/DkTr_0^2, \quad (19)$$

where μ_0^* is Onsager's value

$$\mu_0^*=\mu_0(n^2+2)D/(2D+n^2). \quad (20)$$

From (18) and (19) we finally obtain for the speed of formation

$$\ln k=\ln k_{\kappa=0}+\frac{\epsilon z_B\cos\vartheta_0}{DkTr_0^2}(\mu_0^*-\mu^*e^{-\kappa r_0}/(1+\kappa r_0)). \quad (21)$$

This formula for ion-dipole reactions corresponds to formula (1) in the case of ion-ion reactions.

In the second alternative Eq. (15) has to be integrated to give the resultant probability of formation. In the most general case the critical distance will be a function of the angles ϑ and φ and this functional relation constitutes the "shape of the molecular dipole." It is, however, required that r is, in all directions, larger than a as otherwise ψ_0 is not the valid potential throughout. The further procedure, after (15) has been integrated follows the same lines as above.

It is easy to perform the calculations if r is assumed constant, i.e., between r_0 and $r_0+\Delta r_0$, and if ϑ is unrestricted. This means that the ion has to approach, *in all directions*, the same critical distance r_0. Such a behavior would be rather astonishing for a molecular dipole. As a matter of fact, this assumption leads to the wrong sign for the dependence of k on concentration and dielectric constant.

[5] J. A. Christiansen, Zeits. f. Physik. Chemie **113**, 35 (1924); G. Scatchard, J. Am. Chem. Soc. **52**, 52 (1930); Chem. Rev. **10**, 229 (1932).

[6] It should be mentioned that, according to the kinetic theory, k' is still proportional to $T^{\frac{1}{2}}$ but this is of no importance for what follows.

A more adequate assumption would be that the critical surface is a prolonged spheroid with the dipole in one of the foci directed along the long axis. We have carried through the calculations for this case restricting ourselves to weak potentials (as in the derivation of Debye's Eq. (2)). The result is of a similar nature as (21) and coincides, for small values of κ, with (21). The only difference which remains is that $\cos \vartheta_0$ is replaced by ϵ, the eccentricity of the spheroid. This shows that the result may be chosen with the required sign according to whether the positive or the negative side of the dipole is nearer the surface.

We do not want to stress these calculations which involve a spheroidal form for the following reason. A spheroid would partake of the heat motion with rotations and these would have such a high frequency that the ionic atmosphere would not be able to follow them owing to its considerable time of relaxation.

However, these calculations show that it is legitimate to choose ϑ_0 and r_0 as *critical average values* which are characteristic of the molecule. In this sense we are going to understand them and, consequently, use formula (21).

It will be seen in Section IV that $\cos \vartheta_0$ has to be chosen as $+1$ if we want to obtain agreement with empirical data for positive ions, i.e., an increase of $\ln k$ with an increase of $1/D$. This means, in the spheroidal model, that the negative charge of the dipole has to be nearer the surface if the ion is positive. Furthermore, we assume that the critical distance r_0 coincides with the radius a used in Section II.

Introducing the dimensionless variable

$$z = \kappa a = \kappa r_0 \tag{22}$$

and the dimensionless quantity

$$W = (\ln k - \ln k_{\kappa=0})(2DkTr_0^2)/\epsilon z_B \mu_0^* \cos \vartheta_0 \tag{23}$$

we can write our result in the final form

$$W = z^2/(1+z+z^2/2+(n^2/2D)(1+z)). \tag{24}$$

This formula brings out the dependence of k on concentration in a general way. Whatever the valency of the B ion, and whatever the nature of the other (admixed) ions contributing to the ionic atmosphere, the relationship between W and z ought to be the same.

As for the dependence of the reaction rate on D, the dielectric constant of the solvent, an additional remark should be made. Starting from the idea that $k_{\kappa=0}$, as used above, may still depend on the value of D, several authors[7] have split off from $k_{\kappa=0}$ the part $k_{\substack{\kappa=0 \\ D=\infty}}$ measuring thus the D dependence of k from a point of reference defined by the double transition $\kappa=0$ and $D\to\infty$ (see Eq. (1)). This procedure has proved to be successful in the case of ion-ion reactions. However, in our case it would lead to the result that the change of k with $1/D$ should be in the opposite sense to the change with κ. This is contradicted by all available empirical data.

It should be taken into account that, in our case, the situation is very different from what it is in ion-ion reactions. In the latter case the electric attractions tend towards zero as D increases indefinitely. However, for a dipolar molecule, the "external moment" increases with increase of D. Therefore, though the $\lim_{D=\infty} \mu^*$ exists, the point $D=\infty$ is certainly not an adequate point of reference since it accentuates rather than eliminates the effect of the dielectric constant.

In the case of ion-dipole reactions, owing to the argument just presented, the point $\kappa=0$ can be interpreted as the ideal limiting case in which *all* electrostatic actions have disappeared. For this reason it seems to us that this point represents the adequate point of reference. Anyway we are going to introduce this as a special assumption. Then our formula (21) will express the complete dependence of k on D as on concentration.

Again it is useful to introduce dimensionless variables. If we set

$$\kappa^2 = \lambda^2/D \tag{25}$$

λ will still be of the dimension cm^{-1}, but free from D. Setting then

$$\zeta = \lambda a = \lambda r_0 \tag{26}$$

and

$$W' = (\ln k - \ln k_{\kappa=0})(2kT)/\epsilon z_B \mu_0^* \lambda^2 \cos \vartheta_0 \tag{27}$$

we have the general relation

$$W' = (1/D^2)(1/(1+\zeta/D^{\frac{1}{2}}+\zeta^2/2D)). \tag{28}$$

[7] V. K. LaMer, J. Frank. Inst. **225**, 709 (1938); E. S. Amis and V. K. LaMer, J. Am. Chem. Soc. **61**, 905 (1939); J. C. Warner, Ann. N. Y. Acad. Sci. **39**, 345 (1940).

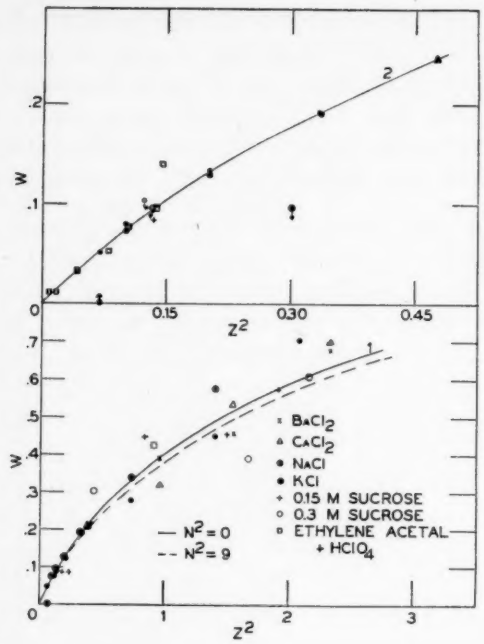


FIG. 1.

It shows that, in the limit $\lambda \rightarrow 0$, W' will change as $1/D^2$. For larger concentrations the increase will become less and depends on the parameter ζ. It should be mentioned that z^2 as well as ζ^2 are, by their definitions (3) and (25), proportional to the ionic strength.

IV. APPLICATIONS

Equation (21) may be tested as to the effect of ionic strength upon reaction rate by putting it into the non-dimensional form given by Eq. (24) and plotting a theoretical curve W *vs.* z^2. As a good approximation the term $(n^2/2D)(1+z)$ may be omitted in making the plot. In Fig. 1 the solid line is the theoretical curve for $n^2=0$ and the broken line that for $n^2=9$. It can be seen that for these extreme values of n^2 the plots do not vary a great amount.

Experimental values of $(\ln k - \ln k_{\kappa=0})$ plotted against ionic strength will confirm the theoretical curve if they can be made to fit it by change of scale, for z^2 is proportional to the ionic strength. From the change of scale of the abscissae a reasonable value of r_0 ought to result. Further, from two given values of $\log k$, corresponding to two given values of W, a reasonable value of the enhanced moment μ_0^* should be calculable according to the relation

$$\mu_0^* = (4.606DkTr_0^2\Delta \log_{10} k)/\epsilon z_B \cos \vartheta_0 \Delta W. \quad (29)$$

In the following calculations $\cos \vartheta_0$ was always chosen as $+1$ (see Section III).

We may test Eq. (21) for the dielectric dependence of the rate by transforming it into the dimensionless form given by Eq. (28), and plotting W' against $1/D^2$. Various theoretical curves will be obtained depending on the value of the parameter ζ chosen. The curves in Fig. 2 are for the two values $\zeta=3.2$ and $\zeta=6.0$. Experimental data agreeing with theory should fit a theoretical curve depending on reasonable values of r_0 and μ_0^*.

There is not a great amount of data available for testing Eq. (21). It is unfortunate that no author has investigated thoroughly the influence of both the ionic atmosphere and the dielectric constant of the solvent upon the rate of any reaction between ions and dipoles.

(a) Dependence on Concentration

In Fig. 1 are plotted on curve 1 the data of Fales and Morrell[8] for the inversion of sucrose in various concentrations of HCl, and the data of Kautz and Robinson[9] for the inversion of sucrose in $0.1M$ HCl containing various concentrations of different salts. In curve 2 of Fig. 1 the part of curve 1 up to an ionic strength of 0.1 has been reproduced and enlarged. In curve 2 has also been plotted the data of Brönsted and Grove[10] for the hydrolysis of ethylene acetal by perchloric acid. The theoretical curves average these points very well. It might be mentioned that in the case of the data of Fales and Morrell the points corresponding to the lowest acid concentrations (below about $0.01M$ C_{H^+}) were omitted since they were entirely inconsistent with the rest of the data. In the case of inversion, observed by Kautz and Robinson, in the presence of NaCl two points are seen to be evidently in error.

In column 2 of Table I are given the r_0 values

[8] H. A. Fales and J. C. Morrell, J. Am. Chem. Soc. **44**, 2071 (1922).
[9] C. F. Kautz and A. L. Robinson, J. Am. Chem. Soc. **50**, 1022 (1928).
[10] J. N. Brönsted and Clinton Grove, J. Am. Chem. Soc. **52**, 1397 (1930).

used in fitting the various data to the theoretical curves in Fig. 1. It will be observed that these values are always reasonable and are always identical for the same type of atmosphere. In column 3 of this table are given the enhanced moments calculated according to Eq. (29). Column 4 contains the value of n^2 (the internal dielectric constant) necessary to reduce the enhanced moment to 3.4×10^{-18} in the case of sucrose[11] and to 4×10^{-18} in the case of ethylene acetal. No value of the moment for ethylene acetal was found recorded in literature so the value 4×10^{-18} was arbitrarily chosen. In the fifth column of this table is a key as to the value of the ionic strength to which this theory held for each charge type of ionic atmosphere. It will be observed that for sucrose inversion, when the atmosphere was made up of univalent ions, the theory held to a value of ionic strength >3 which is as far as the data extended. However, when there were bivalent ions in the atmosphere, the theory applied up to a value of the ionic strength of about 0.6. This is similar to the case of reactions between ions where the presence of higher valence ions in the ionic atmosphere causes a departure from theory at lower ionic strengths than is the case for an ionic atmosphere of univalent ions. The data for the hydrolysis of ethylene acetal extended only to an ionic strength of about 0.08.

(b) Dependence on Dielectric Constant

In two instances there have been extensive studies made of the influence of the dielectric constant of the solvent upon the reaction rate. Amis and Holmes[12] have studied the inversion of 0.1000N HCl catalyzed sucrose in ethyl alcohol-water and in dioxane-water solvents. Since the data for alcohol-water media were shown from energy considerations to be in opposition to the predictions of electrostatics, they would not be pertinent here. However, the data for dioxane-water should fall in line with the requirements of Eq. (21). Dyas and Hill[13] investigated the mutarotation of glucose by HCl in methanol-water solvents. That part of the mutarotation brought about by the oxonium ion is a reaction of the ion-dipole type and should meet the requirements of our theory. The results of these authors are reduced to unit normality.

TABLE I. Constants used in plotting the curves of Fig. 1.

(1) Substances	(2) r_0(A)	(3) $10^{18}\mu_0^*$	(4) n^2	(5) z^2 at ionic strength =1 for curve 1	(6) $k_{\kappa=0}$
Sucrose+HCl +$BaCl_2$	6.0	6.65	1.91	3.867	4.02×10^{-4}
Sucrose+HCl +$CaCl_2$	6.0	9.05	3.32	3.867	4.02×10^{-4}
Sucrose+HCl +KCl	2.5	14.0	6.24	0.670	3.95×10^{-4}
Sucrose+HCl +NaCl	2.5	10.5	4.18	0.670	4.30×10^{-4}
Sucrose (0.15 M) +HCl	3.5	10.3	4.06	1.35	2.17×10^{-4}
Sucrose (0.3 M) +HCl	3.5	7.15	2.21	1.35	2.16×10^{-4}
Ethylene acetal +$HClO_4$	4.0	18.6	7.3 ($\mu^0=4\times10^{-18}$)	1.70	4.15×10^{-1}

[11] E. Landt, Naturwiss. **22**, 809 (1934).

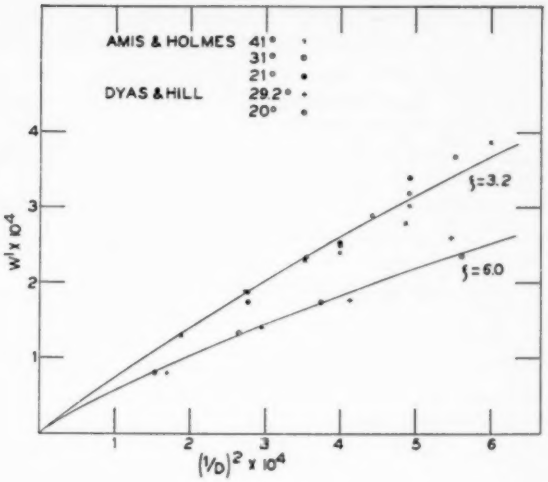


FIG. 2.

In Fig. 2 we have plotted the data of Amis and Holmes and also those of Dyas and Hill. The theoretical curves for $\zeta=3.2$, corresponding to a value of r_0 of about 3.5A used in the calculations on atmosphere effects, averages these data well. However, the values for pure water as the solvent at 21° and 31° were omitted from the graph since they were so inconsistent with the rest of the data that they must be grossly in error. The Dyas and Hill data fitted the same curve remarkably well but led to a r_0 value in this case of only slightly more than 1A. The authors felt that the r_0 value for the glucose-

[12] E. S. Amis and F. C. Holmes, J. Am. Chem. Soc. **63**, 2231 (1941).

[13] H. E. Dyas and G. G. Hill, J. Am. Chem. Soc. **64**, 236 (1942).

TABLE II. Constants used in plotting the curves of Fig. 2.

(1) Substances	(2) r_0(A)	(3) $10^{18}\mu_0$*	(4) n^2	(5) Temp. °C	(6) $k_{K=0}$
Sucrose+HCl	3.5	14.6	6.59	21	4.95×10^{-4}
Sucrose+HCl	3.5	14.7	6.65	31	2.00×10^{-3}
Sucrose+HCl	3.5	14.3	6.42	41	6.76×10^{-3}
Glucose+HCl	2.0	8.07	2.04 ($\mu^0=2\times10^{-18}$)	20	2.95×10^{-1}
Glucose+HCl	2.0	8.13	2.07 ($\mu_0=2\times10^{-18}$)	29.2	7.59×10^{-1}

oxonium reaction would conceivably be less than the r_0 value for the sucrose-oxonium reaction. However, the difference between 1.0A and 3.5A for r_0 seemed rather large, so the choice of an r_0 value of 2.0A gave the very satisfactory results shown by the curve for $\zeta=6.0$ in Fig. 2.

In Table II, column 3 are given the enhanced moments calculated for the sucrose and glucose molecules. The values of μ_0* for sucrose are of the same order of magnitude and compare favorably in actual value with those obtained from the concentration data of entirely different authors when the same value of r_0 is used in the two cases. The μ_0* values for both sugars are very consistent at the different temperatures which is in accordance with theory because in the approximation $(n^2/2D)\ll1$ used by us the ratio μ_0^*/μ_0 depends only on n^2 and, therefore, ought to be independent of temperature. The values of μ_0* in Table I are less consistent; these variations may be due to a change in the nature of the molecule in different surroundings.

Column 4 of Table II contains the value of n^2 for the moment of sucrose to be 3.4×10^{-18} and that of glucose 2×10^{-18}. The latter value was chosen arbitrarily as no value for the moment of glucose was found recorded in the literature. The values of n^2 are very consistent for either molecule, and those values for sucrose compare favorably with values found by the rate dependence upon ionic strength.

It might be pointed out that our derivation of the potential ψ_i in Eq. (8) contains a theory for the activity coefficient of molecular dipoles, analogous to that of Debye and Hückel for ions.

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Internal Rotation in Molecules with Two or More Methyl Groups

KENNETH S. PITZER
Department of Chemistry, University of California, Berkeley, California
July 31, 1942

IN treating the internal rotation of molecules with two or more identical rotating groups, it has been commonly assumed, of necessity, that the potential energy for one rotation is independent of the position of the other groups. For some time the writer has been attempting to study this assumption but until recently the results have been disappointingly negative in character. However, one positive result may now be presented together with a brief discussion of the other work.

Kennedy, Sagenkahn, and Aston[1] have recently published measurements leading to the entropy of dimethyl ether. After subtracting contributions for the other modes of motion, the value 2.65 cal. per degree at 200°K was obtained for the entropy contribution of the two internal rotational degrees of freedom. This was interpreted on the basis of independent potential barriers for each methyl group of magnitude 3100 cal. per mole. However, Ananthakrishnan,[2] has reported Raman shifts of 160 cm^{-1} and 300 cm^{-1} for dimethyl ether. Application of the usual harmonic oscillator formula to these frequencies yields an entropy contribution of 2.63 cal. per degree at 200°K in essentially perfect agreement with the above calorimetric value. Furthermore, these Raman lines have never been explained on any other basis. Therefore it seems likely that these lines are the fundamental frequencies of the two modes of torsional oscillation.

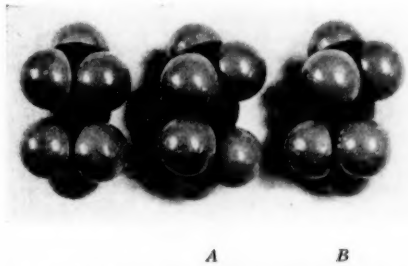
However, this picture is by no means certain. Earlier investigators[3] failed to find one or both of the lines. Although the selection rules permit these torsional modes in the Raman effect, they predict depolarized lines whereas Ananthakrishnan reports both lines polarized. This latter difficulty is partially offset by the fact that depolarized lines are normally broad and both of these lines are reported as broad. Thus additional study is needed before this assignment can be regarded as proved or disproved.

So far as the writer is aware, if this assignment proves to be correct it will be the first set of spectroscopic frequencies for torsional oscillations which is consistent with reliable thermodynamic data. Assuming moderate anharmonicity, these frequencies are in agreement with the observed entropy at higher temperatures and with the observed heat capacity in the gaseous state.[4]

Figure 1 shows first the expected equilibrium configuration and then moderate displacements in each of the two normal modes of internal torsion. It is quite apparent that mode A rapidly brings hydrogen atoms very close together while mode B allows them to remain at considerable distance from one another. Thus it is not surprising to find the first frequency almost double the second. A normal coordinate calculation yields for the force constants: $\partial^2 V/\partial\varphi_1^2 = 8.0\times10^{-13}$, $\partial^2 V/\partial\varphi_1\partial\varphi_2 = -3.4\times10^{-13}$ erg per radian^2. This value of the first constant corresponds to a cosine potential barrier of about 2600 cal. per mole. It is quite evident that the cross derivative or interaction term, although somewhat smaller, is by no means zero.

The other two types of calculations concerning the interactions of two or more methyl groups will now be described briefly. The first concerns the possibility of using the entropy and heat capacity of a single gas to determine both the potential barrier for the rotation of one methyl group by itself and the magnitude of the interaction. Calculations for several typical cases showed that there was practically no chance of obtaining information by this method. The differences were too small to be detected experimentally. This means, inversely, that when potential barriers obtained from entropies are used only to calculate heat capacities, no serious error is likely to arise from the neglect of cross terms.

The second calculation concerned the series propane, isobutane, and tetramethylmethane. A basic entropy was calculated for each molecule using the potential barrier from ethane (2800 cal. per mole) and the best available values for vibration frequencies, moments of inertia, etc. The amounts by which the observed entropies were smaller than these basic values might then be ascribed either to (1) interaction terms such as appear to be present in dimethyl ether, or to (2) a rise in the separate potential barriers upon substitution of methyl groups for the hydrogens in ethane. However, on the basis of reasonable approximations, both assumptions led to the same relative values, 1 to 3 to 6, for the entropy differences in propane, isobutane, and tetramethylmethane.[5] These ratios agree with the observed values within their respective experimental errors. However, this tells us nothing about the presence or absence of the interaction terms.



A *B*

FIG. 1. Left, the equilibrium position; center, moderate displacement in torsional mode A; right, moderate displacement in mode B.

We may then draw the tentative conclusion that thermodynamic data alone will not give definite information concerning cross terms in the internal rotation potential energy, but that spectroscopic data, particularly when coupled with thermodynamic data, have interesting possibilities.

[1] R. M. Kennedy, M. Sagenkahn, and J. G. Aston, J. Am. Chem. Soc. **63**, 2267 (1941).
[2] R. Ananthakrishnan, Proc. Ind. Acad. Sci. **A5**, 285 (1937).
[3] S. C. Sikar, Ind. J. Phys. **7**, 257 (1932); A. Dadieu and K. W. F. Kohlrausch, Monatsh. f. Chemie **57**, 225 (1931); K. W. F. Kohlrausch, *ibid.*, **68**, 349 (1936); M. Wolkenstein and J. K. Syrkin, Nature **139**, 288 (1937).
[4] G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. **8**, 618 (1940).
[5] This calculation may be explained very roughly as follows: (1) The number of interaction terms will be the number of edges of the tetrahedron about the center carbon atom which connect two methyl groups. (2) The increments of potential barrier rise will be, respectively, 1, 2, and 3 for the series, but the number of degrees of freedom are, respectively, 2, 3, and 4. The products of these numbers are thus just double the numbers quoted in the text.

Force Constants and Internuclear Distance

GEORGE GLOCKLER AND GEORGE E. EVANS
University of Iowa, Iowa City, Iowa
July 20, 1942

IN another connection we desired to know the relation between the force constant of the hydrogen-fluorine bond and its internuclear distance not only in HF but also in some of its more complex compounds. An attempt to apply Badger's rule[1] indicated that the modern data of band spectroscopy as summarized by Herzberg[2] permit a very satisfactory estimate to be made of the internuclear distance if the force constant is known. The third-power rule was applied to the hydrides of the elements of the first row of the periodic table as shown in Fig. 1 and Table I. The results are accurate to better than one percent. The molecules studied were divided into three groups: (1) H_2, HD, D_2, and H_2^+; (2) LiH, LiD, BeH$^+$, BeD$^+$, BH, and BD; (3) BeH, BeD, BH$^+$, CH, CD, NH, OH, OD, OH$^+$, and HF. Even better results could have been obtained if the last one had been divided into two subgroups: BeH, BeD, BH$^+$, CH, CD; and NH, OH, OD, OH$^+$, and HF. The first group contains hydrogen atoms only, the second group is made up of molecules all of them in the $^1\Sigma^+$ state, and the third group covers the remainder of the first-row atoms.

TABLE I. Force constant $K=A(R_e-B)^{-3}$ megadyne/cm; R_e in angstroms.

Molecule	State	A	B	Force constant (megadynes/cm) From spectroscopy	From equation	% error
H_2	$^1\Sigma_g^+$	0.1152	0.1555	0.5735	0.5727	−0.14
HD	"	"	"	(0.5728)	0.5728	
D_2	"	"	"	0.5745	0.5718	−0.47
H_2^+	$^2\Sigma_g^+$	"	"	(0.1559)	0.1557	
Li^7H	$^1\Sigma^+$	0.1187	0.5443	(0.1021)	0.1021	
Li^7D	"	"	"	0.1022	0.1023	−0.10
$(Be^9H)^+$	"	"	"	(0.2624)	0.2620	
$(Be^9D)^+$	"	"	"	0.2621	0.2629	−0.31
$B^{11}H$	"	"	"	0.3031	0.3639	
$B^{11}D$	"	"	"	0.3164	0.3667	
Be^9H	$^2\Sigma^+$	0.3003	0.2385	0.2253	0.2229	+1.07
Be^9D	"	"	"	—	0.2231	
$(B^{11}H)^+$	"	"	"	0.3211	0.3225	−0.34
$C^{12}H$	$^2\Pi_r$	"	"	0.4348	0.4383	−0.80
$C^{12}D$	"	"	"	0.4347	0.4399	−1.19
$N^{14}H$	$^3\Sigma^-$	"	"	0.6004	0.5876	+0.21
$O^{16}H$	$^2\Pi_i$	"	"	0.7727	0.7641	−1.11
$O^{16}D$	"	"	"	—	0.7704	
$(O^{16}H)^+$	$^3\Sigma^-$	"	"	0.4855	0.6079	
$F^{19}H$	$^1\Sigma^+$	"	"	0.9626	0.9631	−0.05

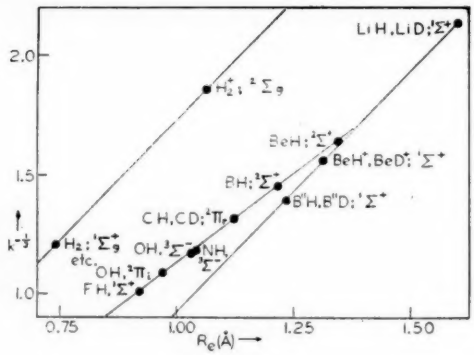


FIG. 1.

The vibrational constant ω_e is not known for Be^9D and $O^{16}D$, but the internuclear distances are, respectively, 1.3427 and 0.969A. Hence it may be predicted from the empirical rule that they are 1527 and 2731 cm^{-1}, respectively. The values of ω_e for $B^{11}H$ and $B^{11}D$ are supposed to be 2366 and 1780 cm^{-1}, respectively, but they are uncertain. While they apparently fit into the third group, it appears plausible from Fig. 1 that these molecules should really belong to the second group. Since their internuclear distances are known accurately (1.2326 and 1.231A, respectively) their vibrational constants ω_e are most likely 2566 and 1890 cm^{-1}, as calculated from their force constants 0.3639 and 0.3667 megadyne/cm which were obtained from the equations of Table I. On the other hand, the ω_e value for $(B^{11}H)^+$(2435.0 cm^{-1}), even though uncertain according to Herzberg, seems satisfactory since the molecule fits onto the straight line of the third group. But $(O^{16}H)^+$ does not fit the graph when the uncertain frequency is used to obtain the force constant. Hence it may be supposed that 3371 cm^{-1} for ω_e of $(O^{16}H)^+$ as calculated from our equation is more satisfactory.

The ion $(Be^9H)^+$ does not fit into group 3, nor do the Li^7H and Li^7D structures. This fact was really the occasion to separate the hydrides into several groups. It appears that the more detailed analysis of Badger's rule has merit and that it can be used to obtain relations between force constant and internuclear distance in the case of first-row hydrides with satisfactory accuracy. It will of course be a matter of considerable interest to see how the predictions made will be fulfilled.

[1] R. M. Badger, J. Chem. Phys. **2**, 128 (1934) and **3**, 710 (1935).
[2] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1928), Table 36.